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Eric Scerri
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Philosophy of Chemistry

Growth of a New Discipline

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Philosophy of Chemistry

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Chapter 1
Introduction

Eric Scerri and Lee McIntyre

It has now been exactly 10 years since the first edition of this volume, *Philosophy of Chemistry: Synthesis of a New Discipline* (Springer 2006) – co-edited with Davis Baird – first appeared as Volume 242 of the *Boston Studies in the Philosophy of Science* series. At that point, the philosophy of chemistry was still an emerging field. Coincidentally it is also 20 years since the two editors of the present volume met at the biennial gathering of the Philosophy of Science Association in 1994 and began a collaboration that resulted in an article which remains the most cited one in the field.[1] Today, we are happy to report that the demand for scholarship in this area has continued to grow, witnessed by the continued success of annual conferences held by the International Society for the Philosophy of Chemistry (ISPC). These meetings have been held every single year, starting in 1997, at different international locations, with the 18th and most recent one at the London School of Economics.[2] Moreover there has been an increased circulation of the journals *Foundations of Chemistry* and *Hyle;* the appearance of numerous books and articles in other venues; and finally the appearance of the present volume.

It seemed only appropriate that in considering a second edition of *Philosophy of Chemistry*, we kept with the founding principle of our earlier book, which was to gather in one place a wide range of new essays in the discipline, comprehensive in

[1] Scerri (1997).

[2] A complete list of these conferences can be found in E.R. Scerri, editorial 46, *Foundations of Chemistry*, 16, 1–2, (2014).

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scope and written by some of the most eminent scholars in the field, to plant a flag indicating not only how far the field has come but where it might be going as well. In recognition of this growth, it is important to point out that over the last decade the philosophy of chemistry has become an increasingly international discipline, drawing special attention from Latin America. Toward the end of the last decade, our publisher came to us with a proposal to translate *Philosophy of Chemistry* into Spanish and we were proud to see *Filosofia de la quimica* appear in 2012. It is our hope that the present volume will match this recognition and perhaps even surpass it by being translated into other languages as well.

A good deal has happened in recent years, including greater acceptance from both the chemistry and the philosophy of science communities. Of course much remains to be done and we hope that this volume will continue to stimulate scholars and educators within these larger fields as well as those within the philosophy of chemistry itself. We cannot deny that a gulf still remains between chemists and philosophers. Chemists favor dwelling on specific details and are seldom quite so interested in the big picture or in reflecting on what their theories and findings generally might mean. At the same time philosophers tend to favor grand generalizations which sometimes means ignoring the grubby details of chemical research. There is always the danger that the philosopher might not have a sufficient understanding of the technical details and might not therefore be taken very seriously by the chemist. This is why continued cross-fertilization and criticism from both sides remains essential to the growth of the field.[3]

In considering a second edition, it was one of our contributors who suggested that we refresh the subtitle – substituting "growth" for "synthesis" – such that the present volume recognizes a link with its past, but moves beyond celebrating a beginning, now that we are two decades out from the founding of the field. Indeed, within these pages readers will find one of the surest signs of maturity in any field: controversy.

One of the most hotly debated questions in the philosophy of chemistry in recent years concerns whether it makes sense to say that chemistry is "ontologically" autonomous from physics. In her paper "The Ontological Autonomy of the Chemical World: Facing the Criticisms," Olimpia Lombardi considers and responds to criticisms that were generated by her earlier paper, in which she put forward the thesis that there *is* a potentially ontological break between chemical and physical phenomena.[4] Both fans and foes of reductionism were thus provoked into action – some claiming that of course chemistry is reducible to physics and others that this particular defense of autonomy gave too much fodder for those who would see *any* kind of emergence claim as spiritual nonsense – generating some of the most interesting scholarship to come out of the philosophy of chemistry in recent years.

[3] Such cross-disciplinary criticism has not occurred to a sufficient degree in our opinion. In addition, philosophers of chemistry have not always responded to criticisms from within their own community. We believe that such a fledgling discipline as philosophy of chemistry can ill-afford such omissions. It is all very well to hold sessions at meetings like the Philosophy of Science Association to air views among the small audiences that typically attend these gatherings. It is another matter to put one's own house in order so as to be of some relevance to the far wider chemical community.

[4] Lombardi and Labarca (2005).

The previous volume included articles on Aristotelean chemistry, Kant's views on chemistry, and the normative-descriptive dimension in philosophy of science. There were articles on chemical modeling, ethics in chemistry, downward causation, the reduction of chemistry and chemical symmetry. More specific issues included periodic systems of molecules, the computer-aided design of molecules and instrumental techniques used in surface chemistry. Finally some more obviously philosophical papers dealt with natural kinds in chemistry, whether or not water is H_2O and the relationship between metaphysics and meta-chemistry.

By contrast the new volume does not repeat any of these topics with the possible exception of the perennial topic of reduction of chemistry to quantum mechanics, but this time by Hinne Hettema, one of the newcomers to the field who did not appear in the earlier volume. Olimpia Lombardi writes about a related topic, that of the ontological autonomy of the chemical world as mentioned above. Another newcomer, Alexandru Manafu, proposes a novel approach to another related issue, that of emergence in chemistry.

There follow three articles by authors who did appear in the earlier volume. Joachim Schummer, the editor of the journal *Hyle* is the author of "The Methodological Pluralism of Chemistry and Its Philosophical Implications." Joseph Earley, turns from symmetry in chemistry to "Pragmatism and the Philosophy of Chemistry". Paul Needham turns from ancient chemistry of Aristotle to a discussion of "One Substance Or More?"

All the remaining authors did not appear in the earlier volume. Rom Harré, the distinguished philosopher, and honorary president of the International Society for the Philosophy of Chemistry, is the author of "Mereological Principles and Chemical Affordances." Farzad Mahootian, writes about metaphor in chemistry and takes up another major theme in recent writing in the field, namely the philosophical nature of the concept of an element. Marina Banchetti-Robino, is the author of many historical-philosophical papers including some on Boyle. In the present volume she examines the move from corpuscles to elements from the writing of van Helmont to Lavoisier. Pieter Thyssen and Koen Binnemans take up another major theme, that of chemical periodicity. Their article examines a particular aspect that proved especially difficult for Mendeleev, namely the accommodation of the rare-earth elements into the periodic table. Although Klaus Ruthenberg, cannot be said to be a newcomer to the field he was inexplicably absent from the earlier volume. This time he was not able to escape and has contributed a study on free radicals in chemistry and the question of realism. Grant Fisher, with whom one of us is currently editing another collection of papers,[5] writes on "Orbital Symmetry, Idealization, and the Kairetic Account of Scientific Explanation." Finally, Jean-Pierre Llored, himself the editor of a monumental two-volume collection of the philosophy of chemistry[6] examines the meaning of ceteris paribus clauses in chemistry.

Our hope is that within this volume, one will find a wide range of scholarship, which represents the best of the philosophy of chemistry. We trust that in the

[5] Eric Scerri, Grant Fisher, forthcoming for Oxford University Press.

[6] Llored (2013).

coming decade our field will continue to grow and prosper and that by now it has earned a place at the table in this series. May we anticipate another *Boston Studies* volume on the philosophy of chemistry in ten (or perhaps fewer?) years' time? If so, the title may already be up for grabs.

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Chapter 2
Reduction for a Dappled World: Connecting Chemical and Physical Theories

Hinne Hettema

2.1 Introduction

The matter of how theories in science relate to each other is a key aspect of the unity of science. For the philosophy of chemistry, this problem is of paramount importance: chemistry and physics are entwined to a degree where it is sometimes difficult, if not impossible, to imagine chemistry with the physics removed. Yet the widespread use of physical theories in chemistry is often not representative of how these theories are used in physics.[1]

This situation raises the question of how these two sciences are related. In the 'received view' on the philosophy of science, the primary connection mechanism between theories is a variety of inter-theory reduction, even while the interpretation of the term reduction could span a range from the relatively liberal scheme advocated by Nagel (1961) to an eliminative scheme advocated by Kemeny and Oppenheim (1956).

In the philosophy of chemistry, it is commonly assumed that the prospects of reduction are rather bleak.[2] The main motivation for this assessment is that the use that chemists make of physical notions quite often violates the uses of these same notions in physics. Yet one of the challenges facing this assessment is the specification of what sort of inter-theory relationships might exist between chemistry and physics in a non-reductive sense.

[1] The resulting disconnects have led some to question the role of physics and theory in chemistry, for instance, in the paper by Hoffmann (2007).

[2] See for instance Woody (2000), Scerri (1998) and Needham (2010) as examples.

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One potential answer is pluralism. Non-reductive, pluralist positions on science have been defended by Cartwright (1983) and Dupré (1993); in the philosophy of chemistry a variety of such a pluralist model is defended by Lombardi and Labarca (2005) and to some degree in Hettema (2012a). Another potential answer is emergence, a point of view that has been defended by Hendry (2006). In addition, alternative notions of the unity of science have been developed, harking back to Neurath's 'encyclopedic project' (see for instance Cartwright et al. (1996) and Potochnik (2011)) on the one hand, or Duhem's notion of 'incorporation' on the other (see for instance Needham (2010)). In addition, Bokulich (2008) has developed a notion of 'interstructuralism'.

A key motivation for these alternatives is that the project of reduction fails because of a fundamental incompatibility – or logical inconsistency – between the theories of chemistry and the theories of physics, which cannot be overcome even by a liberal reading of the Nagelian reduction postulates.

Yet scientific structures can be inconsistent – that is a fact already noticed by Lakatos (1970) and reinforced, though gently, in Priest (2008) (p. 75). The premise of this chapter is that we take such inconsistency as a feature of the inter-theory connection.

The two main questions posed by this stance are of course how we describe such inconsistent structures as part of an overall whole, as well as how science did end up that way. The first one is a descriptive, the latter a 'generative' question. This distinction in descriptive and generative aspects of the problem of inconsistency in science closely mirrors Reichenbach's 1937 distinction between 'context of discovery' and 'context of justification'. We may conclude that as philosophers of science, we have to be capable of dealing with such inconsistent structures from both points of view.

In this chapter, I will develop an approach to solve the generative question, based on belief revision, which may assist in drawing out the inter-theory relations in operation. This essay is motivated by the contention that a revision of Nagelian reduction may rehabilitate the notion of reduction, incorporate a dynamic structure of belief revision in scientific development, and in doing so largely dissolve the distinction between reductionism and pluralism. To be precise, I will argue that Nagelian reductionism is to a significant degree compatible with the pluralist model, and both models can be based on logics that are capably of specifying the intertheory relationships rather precisely.

To be applicable to the reduction of chemistry to physics, I claim that such a revision must on the one hand go back to Nagel's original intention for heterogeneous reduction, and on the other it must draw on fairly recent logical apparatus to stake its claim. My aim in this paper is to rehabilitate the concept of reduction in this sense and argue that the concept is capable, much more capable than was previously thought, of dealing with sciences that are largely autonomous and even inconsistent. I will moreover argue that such cases do not necessarily destroy the unity of science, provided they satisfy some overall criteria regarding how revisions are done. The interesting outcome of this project is that the scope of pluralism is thus limited, and there is a large degree of overlap between reductionist and pluralist positions in the philosophy of chemistry.

The key to my proposed rehabilitation of the reduction relation is twofold. In the first place I argue that a reduction relation is best conceived as a logical *regimentation* or *paraphrase* of what happens when we claim that one theory explains another. Such a position has recently also been defended, from different points of view, by Klein (2009), Fazekas (2009), Dizadji-Bahmani et al. (2010), and van Riel (2011). A more detailed discussion is given in Hettema (2012a).

Secondly, I argue that such a regimentation must be capable of specifying the sort of connections that obtain in the actual practice of science. I argue that that there are several formal mechanisms compatible with the two criteria of the Nagelian scheme.

Belief revision is based on an outright relaxation of the notion of 'derivation', and argues that the 'logical consequence' of which Nagel speaks in his description of the derivation criterion may be satisfied by a relaxed notion of 'consequence'. In this paper I will use a structuralist characterisation of the belief revision relation in terms of the structuralist characterisation of 'conceptual spaces' as advanced by Gärdenfors and Zenker (2011).

I conclude that with these logical moves a notion of Nagelian reductionism is to a significant degree compatible with a pluralist model and a 'dappled world', though not with a world without any unity of science. My conclusion is that it is possible to develop a notion of reduction that is sympathetic to chemistry on the one hand and logically robust on the other. The lesson we may draw from this is that there is not that much that divides reductionist and pluralist approaches in the philosophy of chemistry. This conclusion, I believe, opens up the prospect of fruitful new avenues of research in the philosophy of chemistry.

This paper is structured as follows. In Sect. 2.2 I briefly summarise the important aspects of the Nagelian approach to reduction and some of the recent commentary on this scheme. This development assists in setting the scene for the discussion to follow. In Sect. 2.3 I develop my specific proposals and outline their consequences for a conception of the unity of science. To provide an example of how this might work in practice, I discuss how the proposed structure of reduction *qua* belief revision fits Eyring's theory of absolute reaction rates in Sect. 2.4. Section 2.5 is a conclusion.

2.2 How Liberal Can Nagelian Reduction Be?

As is well known, Nagel (1961) formulates two formal conditions on inter-theory reduction, which can be summarised as the criterion of connectibility and the criterion of derivability. The idea is that terms in the languages of the reducing and reduced theory are connected, and that the laws of the reduced theory can be seen, under a correct connection scheme, to be the logical consequences of the laws of the reducing theory.

However, while Nagel calls these conditions *formal*[3] there is no formal logical 'scheme' to be found in his description. As Dizadji-Bahmani et al. note, the Nagelian model is not committed to a specific regimentation, but rather,

[3] And separates them from a number of informal conditions which he also specifies in great detail.

> Where first order logic is too weak, we can replace it with any formal system that is strong enough to do what we need it to do. The bifurcation of the vocabulary plays no role at all. (Dizadji-Bahmani et al. 2010, p. 403)

Usually, the Nagelian requirements are read as requirements of a first-order logic. On this basis, emendations of Nagel's scheme have been proposed by Schaffner (1967) and Sklar (1967). Causey (1977) argued that reduction postulates must necessarily be *identities*. However, the detailed investigation of *actual* cases of reduction[4] has highlighted that reductions based on identities and derivation which fit this particular logical straitjacket are the exception rather than the rule.

The condition of derivability is formulated in terms of *three* formal requirements for reduction. The three conditions that Nagel mentions in the formal section of the chapter on reduction are that (1) the theories involved can be explicitly stated, (2) the meanings used in the terms are fixed by common convention or by the respective theories, and (3) the statements of the reduced theory are logical consequences of the reducing theory and the reduction postulates.

In combination, the derivability conditions establish the unit of reduction as a scientific *theory* which can be appropriately *paraphrased* (through linguistic formulation in some formal language followed by axiomatisation) so that the right sort of *formal connections* (i.e. logical consequence) can be established.

These conditions do not specify connectibility. To introduce connectibility, Nagel introduces, in addition to the formal requirements, the notion of *coordinating definitions* (which, for clarity, we will call 'reduction postulates' in the remainder of this paper) as an additional assumption. The reduction postulates stipulate a sort of translation manual through

> [...] suitable relations between whatever is signified by '*A*' and traits represented by the theoretical terms already present in the primary science (Nagel 1961, pp. 353–354)

The reduction postulates themselves, however, are far from simple.[5] They allow the language of the theory to be reduced to be connected to the language of the

[4] See for instance Kuipers (1990) for an example of reductions from many sciences, most of which are not based on strict identities.

[5] For instance, Nagel (1961) discussed three kinds of linkages postulated by reduction postulates

1. The links are logical connections, such that the meaning of 'A' as 'fixed by the rules or habits of usage' is explicable in terms of the established meanings of the theoretical primitives in the primary discipline.
2. The links are conventions or coordinating definitions, created by 'deliberate fiat', which assigns a meaning to the term 'A' in terms of the primary science, subject to a criterion of consistency with other assignments.
3. The links are factual or material, or physical hypotheses, and assert that existence of a state 'B in the primary science is sufficient (or necessary and sufficient) condition for the state of affairs designated by 'A'. In this scenario, the meanings of 'A' and 'B' are not related analytically.

reducing theory, or, more interestingly, the language and concepts of the reducing theory to be recast in the language and concepts of the reduced theory.

From here, Nagel's two famous conditions can be formulated as follows:

1. A condition of 'connectability' which stipulates the reduction postulates
2. A condition of 'derivability' which states that the laws or theories of the reduced science are logical consequences of the theoretical premises and coordinating definitions of the reducing science.

The liberal reading of Nagel that I am proposing here depends on the idea that we read Nagel's condition of 'derivability' in the sense of a largely unspecified consequence relation based on a suitable paraphrase of the theories under consideration in some formal language.

The recent reassessments of the Nagelian position (especially the one by Klein (2009) and Dizadji-Bahmani et al. (2010)) read this consequence relation largely in terms of a 'representation' relation, in which the reducing theory can be modified in such a way that it *represents* the concepts of the reduced theory. So, for instance, in the summary by Dizadji-Bahmani et al. (2010), a 'generalised Nagel-Schaffner model' in which the reduction postulates are *factual* claims, is alive and well. They defend the generalised Nagel-Schaffner model against seven specific objections, concluding that none of them apply. In the terminology of Dizadji-Bahmani et al. the generalised Nagel-Schaffner model consists of a theory T_P reducing to a theory T_F through the following steps:

1. The theory T_F is applied to a system and supplied with a number of auxiliary assumptions, which are typically idealisations and boundary conditions.
2. Subsequently, the terms in the specialised theory T_F^* are replaced with their 'correspondents' via bridge laws, generating a theory T_p^*.
3. A successful reduction requires that the laws of theory T_p^* are *approximately* the same as the laws of the reduced theory T_P, hence between T_P and T_p^* there exists an analogy relation.

Two features of this generalised Nagel-Schaffner model are worth noting. The first one of these is that the reduction postulates are part of the *reducing* theory, rather than some auxiliary statements that have a primarily metaphysical import.[6] Secondly, of the three types of linkages that may be expressed by reduction postulates, the first two can be discarded and reduction postulates express *matters of fact*. This is so, because the aim of scientific explanation is, in their words, neither 'metaphysical parsimony' nor 'the defence of physicalism' (p. 405). Thus the Nagelian reading they favor is a naturalised one, in which the aim of reduction is *representability* between the reduced and reducing theory, and confirmation of T_F entails confirmation of T_P for domains where there is significant overlap. In this manner reductions have a high likelihood of occurring where theories have an overlapping target domain.

[6] A similar point was made in a somewhat neglected paper by Horgan (1978), who argues that the reduction postulates supervene on the reducing theory.

The 'idealisations and assumptions' introduced in this model can take on the role of beliefs in a belief revision scheme. This situation reflects actual scientific practice in the (trivial) sense that approximations and idealisations to a complex theory can be seen as various additional beliefs that play a role in the overall scheme.

It is interesting to note that from this point of view we consider the entire reduction *schema* as a key element of the activity of scientific reduction, as opposed to individual *theories* featuring as elements in an abstract reduction scheme which is largely removed from actual scientific practice.

2.3 Structures and Beliefs: Reduction for a Dappled World

In this section, I will consider reduction in the context of a structuralist approach to belief revision based on conceptual spaces. In general, adaptive logics such as belief revision adapt themselves to the situation at the moment of inference. In this, they represent the dynamics of reasoning – a Reichenbachian 'context of discovery' – in which, to save overall consistency, some beliefs are dropped from the overall scheme. I will first briefly characterise the structuralist approach to theories before proceeding with my proposal.

2.3.1 Structuralism Characterised

The structuralist theory approach to scientific theories originates in the work of Suppes (1957) and was given most of its present form in the work of Sneed (1971). It was discussed in detail in Balzer et al. (1987). The key elements of the structuralist theory are summarised in Table 2.1. In the structuralist approach, a scientific theory is characterised as a structure $\langle K, I \rangle$ where K is a structure that characterises the theory 'core' at both the theoretical and non-theoretical level in terms of its (potential) models and partial potential models.

In the structuralist approach, reduction is characterised as a (structural) similarity between structures.

A (specialisation) theory net is a set of structures that are connected through the specialisation relation $\boldsymbol{\sigma}$.[7] The specialisation relation connects a (general) theory to a specialised instance of that theory, which is applicable to a particular situation through the introduction of a special set of limiting constraints. Technically, the specialisation relation can be reconstructed as a constraint condition on the models.

It is interesting to note a strong relationship between the (partial) potential models of a theory and the *conceptual space* of that theory. The (partial) potential models specify the 'language' that is used in the theory, together with some rules for

[7] See Balzer and Sneed (1977, 1978) for an introduction of this relation and the corresponding notion of a theory net.

Table 2.1 Specification of the components of the structuralist conception of theories, cf. Kuipers (2007)

Component	Description
$\mathbf{M}_p$	The potential models, defined as structures of the type $\langle D_1, \ldots, D_k, n_1, \ldots n_p, t_1, \ldots t_q \rangle$ or $\langle D_1, \ldots, D_k, x_1 \ldots x_{p+q} \rangle$
$\mathbf{M}_{pp}$	The partial potential models $\langle D_1, \ldots, D_k, n_1 \ldots n_p \rangle$
$\mathbf{M} \subset \mathbf{M}_p$	The models of the theory, which satisfy all the laws of the theory
$r : \mathbf{M}_p \rightarrow \mathbf{M}_{pp}$	The 'restriction' relation which connects the potential models to the partial potential models
$C \subset \mathscr{P}(\mathbf{M}_p)$	The 'constraint' relation (which will be taken as implicitly present in most of what follows)
$r(\mathbf{M})$	The projected models, i.e. the restriction of the models to the level of partial potential models
$\boldsymbol{K}$	The theory 'core', defined as $\langle M_p, M, M_{pp}, r, C \rangle$
$I \subseteq r(M)$	Weak empirical claim (note that constraints are implicitly assumed)
$I = r(M)$	Strong empirical claim (constraints are implicitly assumed)

its use. This similarity between conceptual spaces and potential models led Kuhn to argue that the structuralist approach was to a high degree compatible with his notion of a paradigm (see Kuhn (1976)) and also forms part of the discussion in Kuipers (2007) on research programmes.

2.3.2 *Belief Revision as Regimentation of Reduction*

As I have outlined in Hettema (2012a), the notion of reduction in the structuralist conception of theories is extraordinarily weak, a weakness which can be turned to strength in cases where we wish to consider the sort of liberal interpretation of Nagel required in the reduction of chemistry and physics. The leading idea in the structuralist conception of reduction is a notion of isomorphism between structures. Beyond that, a number of additional conditions may be imposed, as discussed in Balzer et al. (1987), but the majority of these depend on the *kind* of reduction relation that one wants to defend.

For the purposes of this paper, I will focus on the relationship between AGM theory and the development of conceptual spaces as discussed by Gärdenfors and Zenker (2011).[8] Gärdenfors and Zenker note that the framework of conceptual spaces allows for four types of theory change:

[8] In addition, belief revision has been introduced into the structuralist model by Enqvist (2011). Enqvist develops a highly specific alternative to the notion of 'reduction postulates' qua 'linking commitments' which I developed in Hettema (2012a). Enqvist's construction relies on a construction of specialisation theory nets, to which he applies the AGM belief revision strategies. Enqvist does not fully develop the AGM theory in a structuralist model, and ignores the stratification between theoretical / non-theoretical levels of the theory. In general, developing complex notions in the stratified model adds complications which are usually ignored in the first 'step' of the development of such models, see for instance the development of truthlikeness developed by Kuipers (1992).

1. addition and deletion of special laws (e.g. the creation different models of the theory or the creation of specialisation theory nets);
2. change of scale or metrics as well as the salience of dimensions;
3. change in the separability of dimensions;
4. addition and deletion of dimensions which make up the space

In this context, 'dimensions' refers to the terms in the general structure $\langle D_1, \ldots, D_k, x_1 \ldots x_{p+q} \rangle$ rather than to physical dimensions. In other words, the belief-revision strategies for theory change may involve limited changes of the theoretical cores as modelled in the structures **M**.

In Hettema (2012a) I proposed that we view reduction relationships as an instance of an interstructural *link*, sufficient to establish a global unity of science, but also capable of dropping local 'context'. Belief revision is a stronger theory in the sense that it provides additional specification of how such a link might work.

Abstract links are simply relationships between two sets of potential models (or the 'conceptual spaces') of two theories. An abstract link is defined as (Balzer et al. (1987), p. 61):

Definition 1 (Abstract link) L is an abstract link from $\mathbf{M}_p$ to $\mathbf{M}_p^{'}$ iff $L \subseteq \mathbf{M}_p \times \mathbf{M}_p^{'}$

The leading idea of the abstract link is that it provides a relationship between two different types of potential models, but does little else. In practice, links are instantiated as connection pairs between terms of the 'conceptual space' of one theory to those of another; e.g. $\langle \langle x_i^{'}, x_j^{'}, \ldots \rangle, \langle x_p, x_q, \ldots \rangle \rangle$ that may have some additional restrictions in terms of either values that the quantities can take in the link, or a (law-like) relation between these concepts. The machinery for links can become cumbersome, but the concept is not conceptually complex: it expresses that some terms in one 'conceptual' space can be connected to (a number of) terms in the other conceptual space.

It is possible to define additional properties on links, and in this way develop a concept of interpreting links, reducing links, and so on. Of particular interest is that in the structuralist approach, the unity of science is formulated in terms of theory *holons*, which are large-scale global structures connected by inter-theoretic links. In Hettema (2012a) I have argued that reduction postulates can fruitfully be interpreted in terms of links, and the concept of links can be made to fit the three criteria for reduction postulates that were originally developed by Nagel.

In the remainder I wish to forego many of the details of the structuralist approach by focusing on links as connections between conceptual spaces. The analysis by Gardenfors and Zenker adds structural precision to the generative strategies that are available to establish links. The main import of treating conceptual disconnects in this way, as Gärdenfors and Zenker argue, is that the scope of *incommensurability* between a predecessor and successor theory, or between a reduced and reducing theory, is limited significantly.

From the viewpoint of reduction, this approach is capable of formalising, and subsequently de-fanging, the discontinuity between concepts in the theories of chemistry and the theories of physics. In the next section I will discuss this with the help of a practical example: the theory of absolute reaction rates.

2.4 The Unity of Chemistry and Physics: Belief Revision in the Theory of Absolute Reaction Rates

In this section, I will focus on an example from the chemistry: the theory of absolute chemical reaction rates.[9] This theory is a typical 'chemical' theory in the sense that it draws on many underlying theories to synthesise a new theory. Another motivation is that it can be argued that many of the current problems that plague current philosophers of chemistry – such as the problem of molecular structure[10] and the problem of inconsistent use of quantum theoretical notions – were introduced to accommodate this theory.[11] A brief overview and philosophical evaluation of the theory was given in Hettema (2012b), which I refer to for some of the details.

[9] As the book by Nye (2011) illustrates, this theory was sometimes jokingly referred to as the 'absolute' theory of reaction rates. Many of his contemporaries found Eyring's ideas too radical, as the proceedings of the 1937 workshop at the University of Manchester illustrate. In my earlier paper (Hettema (2012b)) I had this wrong, and used the designation of 'absolute theory' throughout. At the time I was unaware of the earlier ironic use, and thought that 'absolute theory of reaction rates' was a neater choice to designate the theory than the somewhat more clumsy sounding 'theory of absolute reaction rates'. Of course, I now see the error of my ways.

[10] The notion of a (reactive) potential energy surface for the nuclear motion is key to the development of the theory. While the idea was introduced by Born and Heisenberg (1924) and Born and Oppenheimer (1927) it may be argued that the idea of a potential energy surface only reached its full fruition with the development of a theory of chemical reaction rates. The idea of a potential energy surface is part of Wigner's 'three threes' (see below).

[11] Especially illustrative for this is the motivation Eyring (1938) gave for his introduction of various 'semi-empirical' methods in quantum chemistry, which lead to various inconsistencies between these semi-empirical theories and quantum theory.

For the purposes of calculating the potential energy surface for a chemical reaction, Eyring first classifies theories as 'semi-empirical' when they have the following characteristics:

> (a) that each electron can be assigned a separate eigenfunction which involves the coordinates of only this one electron. (b) Multiple exchange integrals are negligible, (c) Normalising integrals for overlapping orbitals are negligible in comparison with unity. (d) The exchange and coulombic integrals for a complicated molecular system may be estimated from a potential curve for the isolated pair of atoms. (e) For distances involved in activation energy calculations this percentage is around 20 per cent. coulombic and 80 per cent. exchange binding, and this varies but little from atom pair to atom pair. (Eyring 1938, p. 8)

Eyring then remarks that more detailed calculations, as well as principled considerations, give no support for the construction of these theories:

> None of these assumptions have been rigorously derived from theory, and, as has been emphasised by Coolidge and James, if one assumes for H_3, the approximate eigenfunctions used by Heitler and London and Sugiura for H_2, the assumptions can all be shown to fail badly. (Eyring 1938, p. 8)

Thus stated, these sort of theories seem to be counterexamples to a theory of reduction: the sort of reduction that derives chemical 'laws' directly from basic quantum theory can only be achieved on the basis of theoretical assumptions that are unjustified from the viewpoint of basic theory and which can moreover be shown up as factually wrong in a large number of practical cases.

A robust and contemporary overview of the theory is given in the book by Glasstone et al. (1941).

The theory of absolute reaction rates was independently developed by Eyring (1935) and Evans and Polanyi (1935), and was the subject of heated debate during the 1930s. In the introduction to the 1937 conference about the theory held at the University of Manchester, the president of the conference in his address remarked that the jury on the 'absolute' theory was still out:

> As to whether these methods are fundamentally sound or unsound is a question the consideration of which belongs rather to the domain of philosophy than to that of chemistry, and it may be necessary to call in an expert in that branch of science to advise us in the matter. (Travers 1938, p. 1)

Somewhat belatedly, it is my opinion that the philosophers of science are, at this point at least, likely to disappoint the scientist, and provide no such advice. Instead, it is the purpose of this last section to use the theory as an illustration of how the theory – whether fundamentally sound or unsound – is a good illustration of how a typical chemical theory functions, and to use it to illustrate the ideas developed in the previous sections.

2.4.1 Overview of the Theory

Glasstone et al. (1941) gives a book-length treatment of the theory. Eyring et al. (1944) discuss the theory in a single chapter, adding a quantum mechanical formulation of the theory. The historical development of the theory is discussed in Laidler and King (1983) as well as in Miller (1998).

Let us now briefly summarise the theory. If we consider a chemical reaction

$$\mathrm{A} + \mathrm{B} + \ldots \leftrightarrow \mathrm{C} + \mathrm{D} + \ldots \tag{2.1}$$

the rate of the reaction is given by Arrhenius law. Arrhenius' law is the main explanatory target of absolute reaction rate theory. Arrhenius' law was developed 1889[12] and writes the rate constants k

$$\mathrm{k} = A \exp(-E/RT) \tag{2.2}$$

expressing the rate constant for a chemical reaction in terms of a 'frequency' factor A and an 'activation' energy E. Several candidate theories were developed to explain Arrhenius' law.

One of those candidate theories was the *collision theory*. In this theory, the 'frequency factor' A in Arrhenius' equation is interpreted as equal to the frequency

[12] The article appears in translated form in Back and Laidler (1967).

of collisions between the reactants. The collision theory assumes that all the reactants are hard spheres, and that any collision that has sufficient energy to reach the activated state will proceed to complete the reaction.[13]

Another candidate was the *thermodynamic* formulation, in which the reaction rate constant is expressed in thermodynamic quantities as

$$\mathrm{k} = \frac{kT}{h} K^{\ddagger} \tag{2.4}$$

Since the equilibrium between the activated state and the reactants is a normal chemical equilibrium it can be related to the thermodynamic theory of chemical reactions, and hence, it can be related to the normal thermodynamic entities free energy, enthalpy ('heat content'), entropy and so forth. This yields a measure of the entropy changes associated with the reaction.

Absolute reaction rate theory is a theory that aims to provide explanations for both the 'activation energy' and the pre-exponential factor A (the 'frequency factor') in the rate equation from first principles. The underlying theories that it uses are quantum mechanics and statistical mechanics. The rate formula of the absolute theory of reaction rates is given in terms of the partition functions Z of the reactants and the transition state by

$$\mathrm{k} = \frac{kT}{h} \frac{Z_{\ddagger}''}{Z_{\mathrm{A}} Z_{\mathrm{B}} Z \ldots} \exp\left(-E_{\ddagger}^{0}/RT\right) \tag{2.5}$$

The advantage of this formulation is that the partition functions for all compounds featuring in the reaction can be calculated using statistical mechanics for vibrational and rotational motion of mechanical systems. While this is still a difficult problem, a detailed consideration of different reacting systems yields a mechanistic insight in how the reaction occurs on a molecular level.

A detailed summary of absolute reaction rate theory was given in Wigner's (1938) presentation at the 1937 Faraday conference, where he summarised the

[13] A modified collision theory often introduces a 'probability factor' P which measures the probability that a collision will lead to a completed chemical reaction. Hence, in the modified collision theory

$$\mathrm{k} = PZ \exp\left(\frac{-E}{RT}\right) \tag{2.3}$$

The 'fudge factor' P is introduced since the collision cross section of a molecule bears no clear relationship to the probability for a chemical reaction. While the collision theory works well for reactions between mono-atomic gases, it breaks down for reactions between more complex molecules. In this respect, the collision theory is not capable of clarifying the internal mechanisms of chemical reactions in the necessary detail.

Table 2.2 Wigner's 'three threes' that characterise transition state theory Wigner (1938)

Three steps in theory of kinetics:	
(WS1)	Determine potential energy surfaces
(WS2)	Determine elementary reaction rates
(WS3)	Solve rate equations for complex reaction mechanism
Three groups of elementary reactions:	
(WE1)	Vibrationally/rotationally inelastic collisions (not a chemical reaction)
(WE2)	Reactive collisions on a single potential energy surface
(WE3)	Electronically non-adiabatic reactive collisions
Three assumptions:	
(WA1)	Electronic adiabaticity: the electronic configuration is in the lowest quantum state for each configuration of the nuclei
(WA2)	The validity of classical mechanics for the nuclear motion
(WA3)	Existence of a dividing surface that trajectories do not re-cross

After Miller (1998)

challenges, types of reactions and assumptions of the theory as a set of 'three threes'.[14] The three threes are summarised in Table 2.2, and translated into a specific set of steps (WS), groups (WG) and assumptions (WA).

Wigner's three steps are: (WS1) The determination of potential energy surfaces, which gives, in the words of Wigner, 'the behaviour of all molecules present in the system during the reaction, how they will move, and which products they will yield when colliding with definite velocities, etc.' (p. 29). The solution of this problem requires the calculation of a potential energy surface, which is a quantum chemistry problem that was solved, somewhat unsatisfactorily, by Born and Oppenheimer (1927).

Wigner classifies the elementary reactions in three groups. Only the second type of elementary reactions can be treated with transition state theory, hence, only (WE2) is considered in the theory.

Finally, Wigner discusses three assumptions (WA). The first specific assumption is the adiabatic assumption (WA1), which assumes that during the reaction the molecular system 'stays' on the lowest possible potential energy surface, and there is no change of electronic configuration. The second assumption, (WA2) is that the motion of the nuclei can be described with classical mechanics, and hence entails the Born-Oppenheimer separation between electronic and nuclear motion. The third assumption, (WA3), is that the reaction does not go 'backwards', i.e. all systems crossing the barrier are reacting systems. The consequence of this is that the step from the reactants to the transition state is the rate determining step for the equation. Once a set of reactants form a transition state, this transition state will fall apart to form the end products of the reaction.

[14] Wigner refers to the theory in this paper as 'The Transition State Method'. The paper by Laidler and King (1983) contains a brief discussion of this conference and the role it played in the subsequent adoption of the theory.

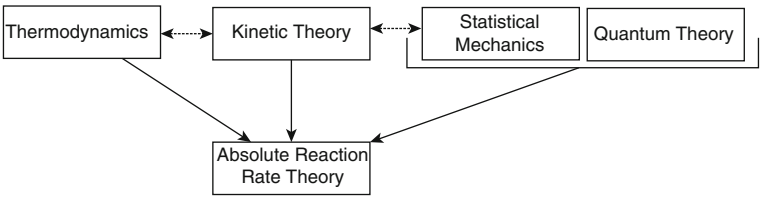

Fig. 2.1 The conceptual structure of the absolute reaction rate theory

As this discussion shows, the theory has two aspects of interest to the philosopher of science:

1. The introduction and specification of a special chemical state, the 'transition state' in terms of a specific location on the potential energy surface of the reaction;
2. The degree to which explanation depends on *comparison* between the collision, thermodynamic, and quantum mechanical/statistical mechanical formulations of molecular quantities.

Hence, the theory of absolute reaction rates has a complex structure which given in Fig. 2.1. The purpose of the theory was to provide exact expressions for the two constants *A* and *EA*. From the viewpoint of *quantitative* explanations for these quantities the theory has been moderately successful, but has, in the words of Laidler and King (1983), 'its difficulties'.

The most interesting aspect of the absolute reaction rate theory is that, again in the words of Laidler and King, it provided a

> [. . .] conceptual framework with the aid of which experimental chemists (and others) can gain some insight into how chemical processes occur. On this score the theory must receive the highest marks; for nearly half a century it has been a valuable working tool for those who are not concerned with the calculation of absolute rates but are helped by gaining some insight into chemical and physical processes. The theory provides both a statistical-mechanical and a thermodynamic insight – one can take one's choice or use both formulations. (Laidler and King 1983, p. 2664)

In this sense, the theory of absolute reaction rates is a very strong example for the unity of science – it is precisely one of those examples where it is hard to imagine a chemistry with the physics removed, but at the same time it is a 'chemical' theory in that it focuses on molecules, molecular structures, and transformations.

2.4.2 Structuralist Characterisation

I have presented a structuralist characterisation of quantum chemistry in Hettema (2012a) and will, for the purposes of this section, draw extensively on the structuralist framework developed there. Since in what follows we will focus on the changes in conceptual space as outlined by Gärdenfors and Zenker (2011) we

only have to focus on the (broad) set of structures M_p, and can ignore many of the finer points of structuralist theorising.

The question is now whether a 'conceptual spaces' approach to the theory of absolute reaction rates is capable of characterising the inter-theory relationships appearing in Fig. 2.1. I will now briefly, and largely informally, discuss the sort of relationships that are at play.

1. The simplest relationship exists between the 'statistical mechanics' 'quantum mechanics' boxes and the theory of absolute reaction rates.

A 'simple' quantum mechanics (of the type I argued that was used in quantum chemistry) is characterised by a Hilbert space and a set of operators as a structure 2_s

Definition 2 (QM-S) x is a characterisation of a simple quantum mechanics, ($x \in 2_s$) if

1. $x = \langle \mathbf{S}, \mathscr{H}, \hat{A}, \sigma(\hat{A}) \rangle$;
2. $\mathscr{J}$ is a system of particles;
3. $\mathscr{H}$ is a separable Hilbert space;
4. $\hat{A}$ is an operator on $\mathscr{H}$;
5. $\sigma(\hat{A})$ is the spectrum of $\hat{A}$.

As was argued by Muller (1998, 2003), quantum mechanics is not easily characterisable in terms of a structuralist model, and, in fact, 'all quantum-mechanical set-structures float in a sea of stories' (Muller 2003, p. 198). As Muller argues, many of the practical applications of quantum mechanics rely on specifications of 'systems', 'measurement' and the like which are fluidly adapted to the situation at hand. All of these adaptations make up the 'sea of stories'.

One such story is quantum chemistry. In Hettema (2012a) I characterised ab initio quantum chemistry as a structure of structures, comprising of a molecular frame, an electronic structure and an atomic basis set. The simple definition is as follows:

Definition 3 x is a potential model for ab initio quantum chemistry ($x \in \mathbf{M}_p$(QCAI)) if there are (sub)structures F, E and B, such that

1. x = (F,E,B,);
2. F represents the molecular frame of the form $\langle \overline{\mathbf{R}}, \mathbf{Z} \rangle$;
3. E represents the electronic structure of the form $\langle \mathscr{P}_e, \mathbf{r}, \boldsymbol{\sigma}, \Psi, \hat{A}, \mathrm{M} \rangle$;
4. B represents an atomic basis set of the form $\langle \overline{\mathbf{R}}_B, \chi, \alpha \rangle$;

For now, it is sufficient to recognise that the connections between a generic ('simple') quantum mechanics and an ab initio quantum mechanics depend on the moves discussed by Gärdenfors and Zenker (2011) in the following sense.

The specification of a molecular 'frame' depends, in the terminology of Gärdenfors and Zenker, on a change of scale or metrics as well as the salience of dimensions as well as on a change in the separability of dimensions. The 'frame'

realises that atomic nuclei are heavier than electrons, and hence have an equation of motion that is to a significant degree separable from the motion of the electrons. From the viewpoint of 'principled' quantum mechanics this makes no difference – all particles form part of the system which must be treated quantum mechanically.

The remainder of the structures, E and B are more specifications of the remainder of the system in the language of simple quantum mechanics – one specifying that the electrons will be treated with the machinery of quantum mechanics, the other specifying the basis in which the quantum mechanical wavefunction will be expanded – they are not overly interesting from a conceptual space point of view.

The links, which I present in detail in Hettema (2012a), express the necessary relationships in relatively complex looking set-theoretic language. The conceptual spaces approach, which I have utilised here, allows for a more intuitive, non-formal characterisation of the same issues.

Eyring's notion of 'semi-empirical' quantum chemistry adds further revisions onto ab initio quantum chemistry by specifying a distinction between 'core' and 'valence' electrons which is unprincipled from the viewpoint of ab initio quantum mechanics, but necessary from the viewpoint of practically implementing the theory without the help of a computer.

2. The connection between statistical mechanics and transition state theory is made by eliminating, from the partition function of the activated complex, the translational component due to the motion along the reaction coordinate (see (Glasstone et al. 1941, p. 189)).[15] This step, however, is captured through the addition of a 'special law' on statistical mechanics, and moreover, this 'special law' characterises the 'transition state' precisely in terms of its degrees of freedom.

Through this specification, the notion of 'transition state', the 'saddle' point on the reactive potential energy surface, can be specified as a 'special law' on top of 'ab initio' quantum chemistry.

3. The comparisons between the thermodynamic, collision and 'absolute' theories are at this stage difficult to determine, since detailed structuralist characterisations of these theories are not readily available. However, one would expect that these characterisations will yield similar insights.

2.4.3 Reduction Postulates and Belief Revision

The characterisations in terms of 'conceptual spaces' can be seen, in the traditional theory of reduction, as reduction postulates which tie the formal paraphrases of the reduced and reducing theory to each other. In particular, the analysis in terms of conceptual spaces allows for a precise characterisation of some of the terminology

[15] A detailed discussion of why this is so falls outside the scope of this paper, but can easily be determined by stepping through the mathematics.

in the generalised Nagel-Schaffner model. Specifically, we can put more precision on the notions of 'typical idealisations', 'boundary conditions', '*approximately* the same' and 'analogy relation', all of which enter into the formulation of the generalised Nagel-Schaffner model.

As a sidenote, the characterisation in terms of this formal framework has additional benefits: it opens the theories of chemistry up to formal treatments in the philosophy of science that focus on other formal aspects of theories such as verisimilitude.

It thus appears that a practical theory of chemistry can, with a little formal help, be reconstructed in terms of philosophical notions such as set theoretic structures and conceptual spaces that are fruitful starting points for the general philosophy of science, and that may have further import for discussions about pluralism and the unity of science.

This result forms a strong motivation for a further study of the theories of chemistry by philosophers of science, and also illustrates that chemistry as a science has interesting philosophical dimensions. Finally, in an attempt to answer the question as to whether 'these methods' are 'fundamentally sound', it may be concluded that they are indeed, though probably not with the methods available to philosophers of science in 1937.

2.5 Conclusion

I have argued that the Nagelian theory of reduction can well be retrofitted to a belief revision approach based on set theoretic structures and conceptual spaces. Doing so leads to a picture of reduction that has interesting consequences for our notions of unity of science. The unity of science under this reconstruction is reconstructed in a 'dappled' sense as a set of specific reasoning strategies that transform 'quantum theory', a generic theory without a firm set-theoretic formulation, into a highly specific theory of chemistry.

It is important to recognise that the belief revision approach is a generative theory, and has a descriptive counterpart – that is, belief revision lets us determine the sort of reasoning that led to a particular model, but is perhaps less capable of describing the end-result with the necessary level of detail. That latter step, however, falls outside the scope of this paper.

It would seem that this approach is capable of reconciling both our intuitions about how reduction should work in practice with actual examples from science, and show that a number of confusing debates in the philosophy of chemistry could have been avoided altogether.

This reconstruction of the notion of reduction fulfills a number of interesting desiderata: it supports the unity of science as an overall epistemic structure, and can make sense of some actual problematic cases of reduction from the philosophy of chemistry. The limitation on incommensurability inherent in this approach also limits the scope of feasible pluralisms in the philosophy of chemistry, and focuses our attention instead on a more precise formal characterisation of the resulting epistemic structures.

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Chapter 3
The Ontological Autonomy of the Chemical World: Facing the Criticisms

Olimpia Lombardi

3.1 Introduction

The explicit defense of the ontological autonomy of the chemical world on the basis of an ontological pluralist view first appeared in a paper by Lombardi and Labarca (2005). Since science has access to reality only through its theories, the metaphysically realist position of God's Eye, according to which scientific knowledge indefinitely approaches the description of reality as it is in itself, was rejected in that paper. From our Kantian-inspired perspective, the object of scientific knowledge is always the result of a synthesis between the conceptual schemes embodied in scientific theories and the independent noumenal reality. However, unlike Kantian theses, our position admits the existence of different conceptual schemes, both diachronically and synchronically, and this leads to an ontological pluralism that allows for the coexistence of different, even incompatible ontologies.

When the ontologically pluralist perspective is applied to the relationship between chemistry and physics, a picture completely different from the traditional one appears. Once the epistemological irreducibility of chemistry to physics is admitted, the ontological priority of the physical world turns out to be a mere metaphysical prejudice. From the pluralist viewpoint, concepts like bonding, molecular shape and orbital refer to entities belonging to the chemical ontology, which only depends on the theory that constitutes it. Chemical entities do not owe their existence to an ontologically more fundamental level of reality, but to the fact that they are described by theories whose immense predictive and creative power cannot be ignored.

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The original 2005 paper, as well as the subsequent works (Lombardi and Labarca 2006, 2011; Labarca and Lombardi 2008, 2010a, b), had a fast and relevant impact, and received both support and criticism. More than eight years after that original work, it is time to take into account those criticisms and to try to answer them. This is the main purpose of the present work.

3.2 The Concept of Ontological Reduction as an Obscure Notion

The first criticism came immediately from Paul Needham (2006), who rejected the very notion of ontological reduction that underlies those positions to which ontological pluralism is explicitly confronted. He called into question the coherence of the idea of ontological dependence: "*Is this idea of second class existence*, *in what the authors go on to describe as* '*an ontologically inferior level of reality*', *coherent*?" (Needham 2006, p. 75). For the author, the notion of ontological reduction is not sufficiently clear to be seriously considered: "*What is needed to make the thesis clear is an acceptable notion of ontological dependence*, *in terms of which the ontology of the reduced theory can be said to be dependent on that of the reducing theory*, *but not vice versa*" (Needham 2006, p. 78; see also Needham 2010). But, according to Needham, the onus of proof falls on the shoulders of the ontological reductionist, who must give a coherent account of his position; until he does not do it, we do not need to spend our time in ontological matters. With respect to this issue, Hinne Hettema seems to agree with Needham when he claims that "*the notion of* '*ontological reduction*' *standing on its own is nonsensical*" (Hettema 2012, p. 382) and proposes that "*philosophers of chemistry better rid themselves of the concept of* '*ontological reduction*'." (Hettema 2012, p. 409).

I strongly disagree with these standpoints, where the notion of ontological reduction is deprived of philosophical sense. On the contrary, both ontological reduction and ontological dependence have been recurrent themes in the history of philosophy.[1] Already in the Pre-Socratic philosophy, the idea of a fundamental stuff (water, apeiron, air) of which everything is made was the trademark of the Milesian school (Thales, Anaximander, Anaximenes) in its quest for the reduction of multiplicity to unity. And although this initial monism was later abandoned in favor of an ontological picture based on a handful of material principles, the attempt to reduce the diversified empirical reality to a simpler underlying realm survived in Empedocles and his four elements (fire, air, water and earth) and in the atomism of Leucippus and Democritus (with their atoms and the void).

In Plato's philosophy the principles became non material. Nevertheless, certain ontological items, the Ideas, retained ontological priority over the others in the sense that they did not need anything else to exist; the remaining items had a

[1] The response to this criticism was barely suggested in the article devoted to answer Needham's objections (Lombardi and Labarca 2006).

secondary existence since they required the primary items to exist – sensible things were mere "copies" of Ideas.

In the Modern Age, the notion of ontological dependence reappeared in two senses. On the one hand, the relationship between primary qualities, endowed with ontological priority, and secondary qualities, which were merely subjective, permeated the philosophy of Locke and the physics of Galileo. On the other hand, Ancient atomism, first introduced in Modern Europe by Gassendi, was reborn in Boyle's corpuscular philosophy. In turn, corpuscularism strongly influenced later physics, such as Newton's corpuscular theory of light. The influence of Ancient atomism arrived to the nineteenth century through John Dalton's modern atomic theory.

Still closer to our times, two of the most famous physicists of the late nineteenth century devoted much of their intellectual effort to reduction. Under the assumption that gases are nothing else than particles in mechanical interaction, Boltzmann tried to explain thermal phenomena in gases in terms of classical mechanics. Meanwhile, Maxwell devoted much of his scientific work to the reduction of electromagnetic phenomena to mechanical vibrations of a luminiferous aether. In both cases, the underlying ontological assumption was that Nature is made of mechanical entities, which are governed by the laws of physics as first discovered by Newton; it was precisely this assumption that justified the strategies directed to explain the new theories (thermodynamics, electromagnetism) by means of classical mechanics.

Nowadays, ontologically reductionist ideas are still present in many areas of science. Perhaps the most striking example is the present-day particle physics as embodied in the Standard Model. The need of huge investments to build immense particle accelerators, in particular, is usually justified in ontologically reductionist terms: those accelerators are necessary to conclude the task of discovering those tiny elemental entities of which the entire reality is composed. This ontological picture is clearly summarized by Fritz Rohrlich: "*chemistry tells us that a piece of wood is 'really' a complicated arrangement of many kinds of molecules bound together*; *atomic physics tells us that molecules are 'really' various atoms held together by interatomic forces*; *particle theory tells us that atoms are 'really' elementary particles in interaction*, *and so on*" (Rohrlich 1988, pp. 295–296).

These are only some of the many examples which show that the concepts of ontological reduction and of ontological dependence are completely meaningful and have a venerable tradition in the history of philosophy and of science. On the basis of this tradition we, as philosophers of science, are entitled to use them, even with the purpose of rejecting ontological reductionism.

3.3 Criticisms from a Non-pluralist Perspective

An author who does not deprive ontological matters of meaning is Lee McIntyre. He acknowledges that the original argument in favor of the ontological autonomy of the world of chemistry "*caused quite a splash in the field and is the subject of much current debate*" (McIntyre 2007a, p. 292). Moreover, he proposes to examine not only

the epistemological but also the ontological commitments that lie behind the concepts of reduction and emergence (McIntyre 2007b). However, following a perspective that has become traditional in the recent philosophy of chemistry, McIntyre accepts with almost no argumentation that chemical regularities are ontologically dependent upon underlying physical relationships. He therefore focuses his interest on the merits of the epistemological interpretation of reduction and emergence.

From this perspective, McIntyre rejects ontological pluralism as a "*bold claim*" (2007b, p. 340). According to the author, the reasons for advocating the ontological autonomy of the chemical world are not sufficient since they are based on insights about descriptions: "*If they are right that reductive explanation depends on descriptions, it is unclear why this would need to reach all the way to ontology*. [...] *Descriptions are important, but I believe that they need not force us to reconstruct ontology*" (McIntyre 2007b, p. 340).

Of course, there are no empirical methods to endow ontological claims with a definitive verification. The ontological reduction of the ontology A to the ontology B, or even the ontological emergence of A from B, is usually expressed in counterfactual terms as 'if B didn't exist, then A wouldn't exist'; but there is no way to decide the truth value of a counterfactual proposition beyond any doubt. So we always rely on indirect arguments to justify our commitment to an ontological thesis like that. In particular, what happens in the epistemological domain can offer good arguments for our ontological conclusions. In this case, we assess the ontological counterfactual on the basis of the acceptability of its epistemological counterpart: 'if the theory describing B were wrong, then the theory describing A would be wrong too'. This is no longer an ontological claim, but a claim about what effectively happens in science, and its truth value depends on the particular relationships between the two theories. And there are good scientific arguments to believe that such an epistemological sentence is false; as Jaap van Brakel explicitly asserts: "*If quantum mechanics would turn out to be wrong, it would not affect all* (*or even any*) *chemical knowledge about molecules* (*bonding, structure, valence and so on*). *If molecular chemistry were to turn out to be wrong, it wouldn't disqualify all* (*or even any*) *knowledge about, say, water*" (van Brakel 2000, p. 177).

However, from a non-pluralist realism a further argument against ontological pluralism can be posed: the history of science supplies many examples of successful intertheoretic relationships that have been interpreted in ontologically reductionist terms, and such success is the best proof of ontological reduction. For instance, temperature is nothing else than mean kinetic energy because, if this were not the case, the identity of numerical values between the corresponding magnitudes would lack explanation (McIntyre, personal communication). This inference, when viewed in a wider context, is a version of the "*no-miracle argument*", that is, an inference to the best explanation appealed to by scientific realists to support their position: the truth of a theory is the best explanation of its empirical success because, without such a truth-based explanation, that success would be a miracle. In Putnam's words: "*The positive argument for realism is that it is the only philosophy that doesn't make the success of science a miracle*" (1975, p. 73). When transferred to the discussion about intertheoretic relationships, the argument reads: ontological reduction is the best explanation of the empirical success of

intertheoretic relationships because, without a reduction-based explanation, that empirical success would be a miracle.

As it is well known in the context of the general philosophy of science, the no-miracle argument has received different and weighty responses, all of them directed to show that empirical success is not a sufficiently good argument for truth. One of them is based on the so-called 'Duhem-Quine thesis' about the *underdetermination of theory by evidence* (Duhem 1906; Quine 1951): two theories may be empirically equivalent – and thus equally successful from the empirical viewpoint – but ontologically incompatible and, therefore, they cannot be both true. Another objection raised against the no-miracle argument, which is particularly relevant to our discussion, is the *pessimistic meta-induction*, which shows that many theories considered successful in their own times were later finally discarded. For instance, Larry Laudan (1981) reports historical cases of scientific theories that, in spite of their success in the past, are considered false at present. As a consequence, there is no reason to believe that our present best theories will not have the same fate. The general conclusion is that empirical success does not guarantee truth.

The pessimistic meta-induction can be easily transferred to the intertheoretic case: analogously to the historical answer in the original context, the history of science also shows how intertheoretic links, empirically successful at a certain time, were sometimes later replaced due to the modification of one of the poles of the relationship. The paradigmatic example is the link between thermodynamics and the theory describing the supposedly underlying domain. In this case, the "fundamental" theory changed – from caloric theory, to classical mechanics and, finally, to quantum mechanics – and the intertheoretic links changed with it; however, the "phenomenological" theory – macroscopic thermodynamics – remained immune to the modifications during the entire historical process. Therefore, on the basis of the intertheoretic version of the pessimistic meta-induction, we can conclude that there is no reason to expect that our best intertheoretic relationships will not be abandoned in the future because of the failure of the supposedly fundamental theory. The general conclusion in this case is that the empirical success of an intertheoretic relationship is not sufficient to support the assumption of the ontological reduction of some entities to others more fundamental.

What is more, in the case of the relationship between chemistry and physics, the claim of ontological reduction is even weaker due to the epistemological irreducibility of the theories of chemistry to the descriptions supplied by physics. In this scenario, the insistence on the ontological dependence of chemical entities and regularities upon the physical domain is not justified: the burden of proof lies on the non-pluralist realist.

3.4 The Role of Practice of Science

In a brief and very well written article, Alexander Manafu (2013) discusses, from a general viewpoint, the proposal advanced in the original work on ontological pluralism (Lombardi and Labarca 2005). The author does not call into question

the pluralistic proposal; his purpose consists in stressing that the appeal to internalist realism (Putnam 1981) is not sufficient, by itself, to justify the ontological autonomy of the world of chemistry.

After appropriately reconstructing the theses of the original 2005 article, Manafu accepts that there is no theory-independent ontology and admits the possible coexistence of different conceptual schemes. However, according to him this is not sufficient to conclude that two different conceptual schemes applying simultaneously to the same portion of "noumenal" reality will always define different ontologies. He points out that, in order to draw this conclusion, one needs to argue that the ontologies defined by different conceptual schemes have, in Quine's terms, the same "ontological rights" (Manafu 2013, p. 227). In other words, it is necessary to show that the various conceptual schemes are equally legitimate, none being privileged over the others. However, this may not be the case in two different situations. First, "[t]*wo different conceptual schemes may differ with respect to their theoretical virtues*: *one may be simpler*, *more systematized*, *or it may have more explanatory pow*er." (Manafu 2013, p. 227). In this situation, the ontologies constituted by those conceptual schemes will also differ with respect to their ontological rights. Second, "*conceptual schemes need not be logically independent from one another*. *For example*, *if one conceptual scheme can be deduced from another with the help of correspondence principles relating the terms of the two theories*, [. . .] *the claim that different conceptual schemes define distinct ontologies becomes problematic*" (Manafu 2013, p. 227). It is quite clear that in this situation it is not admissible to deny the ontological priority of one of the domains over the other. On this basis, the author concludes that "*different conceptual schemes do not always* (*or do not necessarily*) *define different ontologies*." (Manafu 2013, p. 226).

Strictly speaking, Manafu's argument is completely correct, even with respect to the Kantian-rooted ontological pluralism that improves the internalist position of the original 2005 paper (see Lombardi and Pérez Ransanz 2012). However, it does not dismantle our pluralist conclusions about the relationship between chemistry and physics. I will analyze separately each of the two situations mentioned by the author.

Let us begin with the second situation considered by Manafu. Although it is true that a relation of deduction between conceptual schemes blocks ontological autonomy, this is not the kind of relation that can be found in the chemistry-physics case. Manafu's argument takes the conclusion we draw in our original article (Lombardi and Labarca 2005) out of context. In fact, that work began by reviewing the broad consensus among philosophers of chemistry about the epistemological irreducibility of chemistry to quantum mechanics. And precisely on that basis we asserted that "[i]*f chemical concepts could be epistemologically reduced to quantum concepts*, *there would be a good reason to believe in the ontological reduction of the chemical world to the ontology of quantum mechanics*. *But when the epistemological irreducibility of chemistry is accepted*, *there is no argument other than metaphysical realism for postulating ontological reduction*" (Lombardi and Labarca 2005, pp. 139–140).

In other words, if the theories of chemistry could be deduced from the "fundamental" theories of physics, as some of the founding fathers of quantum mechanics believed (see Dirac 1929), ontological pluralism would not apply to the case of the relationship between chemistry and physics. But most of the work of the last decades in the philosophy of chemistry has pointed precisely towards the opposite direction, by stressing that the deductive links required by the traditional views of reduction (Kemeny and Oppenheim 1956; Nagel 1961) cannot be established between the two theoretical domains. Therefore, the ontological autonomy of the chemical world can be legitimately argued for on the basis of ontological pluralism.

With respect to the first situation put forward by Manafu, it is true that two different conceptual schemes may differ with respect to their "theoretical virtues". However, when the theories of chemistry and physics are compared, it is not clear at all that, say, quantum mechanics is simpler, more systematized or that it has more explanatory power than molecular chemistry. Moreover, considering *pragmatic virtues* is even more interesting in the comparison of theories: some conceptual schemes may lead to more successful theories with respect to what Ian Hacking (1983) calls the *intervention* on reality. As this author claims, in the discussions about the foundations of science we have paid too much attention to theoretical considerations, forgetting the effective practice of science: it is in this pragmatic context that the criterion for the existence of scientific entities has to be searched for. According to Hacking, we accept the existence of unobservable entities when we can "spray them", that is, when we can use them for intervening in other aspects of nature: "*We are completely convinced of the reality of electrons when we set out to build – and often enough succeed in building – new kinds of devices that use various well-understood causal properties of electrons to interfere in other more hypothetical parts of nature*" (Hacking 1983, p. 265). In other words, it is scientific experimental practice, and not descriptive matters about theories, which gives us the best support for our commitments about scientific reality.

This shift in perspective proposed by Hacking has been taken into account in the context of ontological pluralism in recent works (Labarca and Lombardi 2010a, b; Lombardi and Labarca 2011; Lombardi and Pérez Ransanz 2012), by arguing that the conclusions about the existence or non-existence of chemical entities are no longer grounded exclusively on considerations about intertheoretic relationships. From this pragmatic viewpoint, "*molecular chemistry holds the winning card*: *its astonishing success in the manipulation of known substances and in the production of new substances is the best reason for accepting the existence of the entities populating its realm. In other words*, *we are entitled to admit the reality of the molecular world – inhabited by*, *among others*, *chemical orbitals*, *bonding*, *chirality*, *molecular shapes – on the basis of the impressive fruitfulness of molecular chemistry itself*, *independently of what physics has to say about that matter*." (Lombardi and Labarca 2011, p. 74). As a consequence, not only the theoretical virtues, but primarily the pragmatic virtues of chemistry are the facts that play a decisive role in the arguments for the ontological autonomy of the domain of

chemistry. It is interesting to notice that, when the relevance of the praxis of science is considered, our ontological pluralism is not far from the *practical realism* defended by Rein Vihalemm (2003, 2005, 2011) in several works: even if there is an external, noumenal world, the different scientific ontologies are captured by the conceptual schemes presupposed by those theories accepted due to their pragmatic virtues.[2]

Summing up, although the argument developed by Manafu in his article has no logical fissures, neither of the two situations considered by the author turns out to be a serious obstacle to defend the ontological autonomy of the chemical world on the basis of our ontological pluralist perspective.

3.5 The Continuity Between Chemistry and Physics

In a paper devoted to discussing the problem of the existence of the orbitals,[3] we speak of a *conceptual breakdown* or *conceptual discontinuity* between molecular chemistry and quantum mechanics: "*Whereas in quantum mechanics 'orbital' is a non-referring term, in molecular chemistry orbitals exist as spatial regions on the basis of which the shape of the local and individual molecules can be explained*" (Labarca and Lombardi 2010a, p. 155). In that paper we stress that, in the last decades, many authors have recognized the conceptual discontinuity between the two theories (Woolley 1978; Primas 1983, 1998; Amann 1992). More recently, Hinne Hettema (2012, p. 368) talks about the "*ontological discontinuity*" between the terms of chemistry and those of physics: certain terms used both in chemistry and in physics seem to refer to different items in the two disciplines. According to this author, such discontinuity is "*one of the central problems in the philosophy of chemistry, around which many other problems, such as that of reduction, revolve*." (Hettema 2012, p. 368).

Peter Mulder (2010, 2011) also admits that the term 'orbital' has two different scientific meanings. On the one hand, "[t]*he term 'orbital' applies to one- electron wave functions in general, of which hydrogenic orbitals are merely a subset*" (Mulder 2010, p. 178). However, he also acknowledges the use of the term to denote a region of high electronic density: "*the point should be clear that the understanding of orbitals as regions of electron density is pervasive in chemistry*." (Mulder 2011, p. 31). Nevertheless, Mulder disagrees with us with respect to

[2] This does not imply the agreement with Vihalemm's defense of Niiniluoto's (1999) critical scientific realism (for a criticism of Niiniluoto's position, see Lombardi and Pérez Ransanz 2012, Chapter 2).

[3] Here I will not discuss the particular issue of the existence of orbitals, since the detailed treatment of the problem is beyond the limits of this paper and will be treated in a future work (for a discussion of this topic, see Scerri 2000, 2001, 2002).

the discontinuity between these two meanings, which for us is a result of the conceptual breakdown between molecular chemistry and quantum mechanics.[4] According to him, "*if there is indeed any kind of* "*conceptual breakdown*" (Labarca and Lombardi 2010a, p. 155), *it appears* within *quantum mechanics*, *equally affecting the quantum-mechanical and chemical meaning of* '*orbital*'." (Mulder 2011, p. 33), and it is due to the use of approximations, in particular the suppression of all interactions except those with the nuclei at relatively fixed nuclear positions: "*Approximations are therefore made within quantum mechanics*, *as a result of which the quantum-mechanical concept of an orbital arises*." (Mulder 2011, p. 33). Moreover, "*the meaning of* '*orbital*' *as a region of high probability density follows quite straightforwardly from its meaning as a wave function*. [. . .] *The two concepts are therefore continuous with one another*." (Mulder 2011, p. 33).

It is interesting to analyze this criticism because it brings to light the difference between two kinds of approximations, those that remain confined in the conceptual context of a discipline, and those leading to a conceptual breakdown. When, in the domain of classical mechanics we study the motion of a body on a surface with very low friction, we are entitled to approximate the situation to another with no friction which, although non-existent in the empirical world, is an admissible situation in classical mechanics. On the contrary, if we suppose that a very fast particle moves at a speed exceeding the speed of light – an assumption completely legitimate in the classical domain–, we introduce a conceptual breakdown with respect to special relativity: the state of affairs resulting from the assumption contradicts one of the principles of the theory itself.

In the case of the application of quantum mechanics to the description of molecules, the suppression of interactions between electrons is an approximation that remains within quantum mechanics. But this is not the case when, as is usual in chemistry, the electronic density – computed by squaring the amplitude of the wavefunction of an electron – is interpreted as a kind of mean value of the definite positions occupied by the electron in its motion around the nucleus: "*If a series of measurements could be made of x without disturbing the motion of the*

[4] We will not discuss the charge of "*incoherence*" that Mulder directs to our position (Labarca and Lombardi 2010a), since the charge is based on the fact that we supposedly "*maintain that in chemistry as well*, *electrons do not have definite trajectories*, *i.e. no definite positions at all times*." (Mulder 2011, p. 32). Since Mulder does not cite the criticized claim, and fails to indicate the page number, it is hard to understand where he could have drawn this conclusion from. In fact, we take just the opposite position: whereas quantum items are not spatially localized individuals, electrons in chemistry – although ruled by a law that fixes their position only statistically – are individual objects in a classical sense. Perhaps Mulder's conclusion is due to the fact that we say that "*electrons do not follow definite orbits*" (Labarca and Lombardi 2010a, p. 154). But this does not mean that "chemical" electrons do not follow definite trajectories, since not every trajectory is an orbit; an orbit is a closed trajectory which, in general, is governed by a simple law. By contrast with Mulder's reading, we claim that, although chemistry does not adopt a planetary model of the atom where electrons follow definite orbits, electrons are still conceived as individual and local objects with a definite spatial position.

particle, *the resulting distribution would be* ρ. *The latter would then reflect the motion of the particle in the same way in which the density of the image on a long-exposure photograph reflects the motion of a macroscopic object*." (Nelson 1990, p. 643).[5] However, this picture is not the consequence of an innocent approximation: it is based on the assumption of individual objects with definite positions, whose existence is in contradiction with the non-individuality of quantum systems resulting from the principles of the theory. Therefore, the transition from the concept of orbital as wavefunction to the concept of orbital as a spatial region of high electronic density is not a continuous transformation within quantum mechanics, as Mulder claims, but a conceptual breakdown with respect to the theory that is supposedly "fundamental".

The concept of orbital is not the only theoretical element where the conceptual discontinuity between molecular chemistry and quantum mechanics becomes manifest. By separating the wavefunction of the molecule into its electronic and its nuclear components, the Born-Oppenheimer approximation makes it possible to compute the energy levels of even very complex molecules. The Born-Oppenheimer approximation proceeds in two steps. The first step is often referred to as "*the clamped nuclei approximation*": the electron-nucleus interactions are conceived of in terms of electrons in the Coulomb potential produced by nuclei "clamped" at definite positions. (for a detailed discussion of the implicit assumptions underlying the Born-Oppenheimer approximation, see Lombardi and Castagnino 2010). But the assumption of particles – the nuclei – with definite values of momentum and of position is at odds with the Heisenberg principle, which prevents a quantum system from simultaneously having definite values of non-commuting observables. In other words, the clamped nuclei approximation introduces a conceptual breakdown with respect to quantum mechanics, just as a speed exceeding the speed of light makes it with respect to special relativity.

In conclusion, the approximations generally used to link molecular chemistry with quantum mechanics are not confined "within" quantum mechanics; on the contrary, they bring in a discontinuity between the concepts of the two domains, and such discontinuity prevents those concepts from being interpreted as referring to the same ontological item.

Despite having claimed the continuity between the quantum-mechanical and the chemical meanings of the term 'orbital', Mulder expresses his worries about how electrons are conceived in chemistry: "*Does this mean that chemistry is 'false' because it regards electrons as individuals*? *I think that one has to concede that to the extent that chemists speak of electrons as individuals*, *what they say is indeed not literally true*." (Mulder 2011, p. 32). According to the author, "*individualism about electrons in chemistry*" has a merely pragmatic character, whereas

[5] Nelson's statement is cited by Mulder in his 2010 paper. However, here the author seems to "forget" what he says in his 2011 paper, where he admits that the term 'orbital' has two different meanings. From a more decidedly reductionist position, in his 2010 paper Mulder considers Nelson's position simply wrong: the chemical view of orbitals is a misconception.

"*non-individualism in quantum mechanics*" is a result of the philosophical analysis of the mathematical formalism (Mulder 2011, p. 33). Here we see a clear declaration of an ontological reductionism that makes chemistry a secondary discipline: whereas electrons are really as described by quantum mechanics, their treatment in molecular chemistry is strictly false and only pragmatically useful. In other words, chemistry supplies only helpful tools, but the description of the "true reality" is a task of physics. However, this is not a criticism of ontological pluralism; it is the mere statement of a position that the ontologically pluralist perspective rejects outright.

Independently of the particular criticisms directed by Mulder to our defense of the ontological autonomy of chemistry, it is interesting to wonder why the author finds it necessary to direct his efforts at arguing for the continuity between chemistry and physics. And this leads us to the issue of the following section.

3.6 The Fear of a Disintegrated Science

In his critical commentary on ontological pluralism, Needham conceives the different but equally theory-dependent ontologies "*as in some sense at odds with one another so that they can't simply be amalgamated into one all-embracing ontology*" (Needham 2006, p. 73). On this basis, he considers our philosophical position as an "unpalatable remedy" for facing the problem of the secondary status of chemistry with respect to physics. Now, it is true that ontological pluralism stands in open conflict with the metaphysical idea of an all-embracing ontology under which any particular ontology could be subsumed. Nevertheless, this does not amount to conceiving the different particular ontologies as being at odds with one another. Needham seems to be afraid of a kind of ontological disintegration, which would lead us to a fragmentary science where the different disciplines, and even the different theories, are completely disconnected from each other. As we will argue, the threat of fragmentation can be averted from a non-reductive idea of unification.

Although not in direct dialogue with the Kantian-rooted ontological pluralism, this fear of fragmentation is also present in the recent book of Hettema (2012), where the author explicitly advocates for a reductionist view of the relationship between chemistry and physics: "*The reduction of chemistry to physics is in this sense indeed a paradigm case for the notion of reduction*" (Hettema 2012, p. 410). But it is surprising that, to reach this conclusion in the last sentence of his book, Hettema has driven us through the long road of the complexities and difficulties that underlie the supposed reduction. In fact, according to the author, intertheoretic links do not supply a global reduction, but only local and partial reductions of certain particular theories of chemistry; in turn, they introduce idealizations and approximations that establish weak and discontinuous connections between theories. Furthermore, those connections remove certain concepts from their primary context

in a manner that sometimes proves to be unacceptable from the viewpoint of the theory to which they originally belong. In this way, intertheoretic links transform the reducing theory with assumptions external to and frequently incompatible with that theory itself. Hettema acknowledges that these links supply a notion of reduction so liberal that it could even be made compatible with non-reductionist positions. But once the concept of reduction has been relaxed in such a way, we are entitled to ask why the relationship between chemistry and physics is still called 'reduction' instead of 'inter-theory link'.

The answer to this question relies on the defense of the unity of science, which is viewed as a "corollary" of the notion of reduction (Hettema 2012, p. 11): "*reduction originated as a primary glue in the unity of science. Hence reduction has a strongly programmatic aspect, which has consequences not only for the individual status of theories, but also for how theories hang together*" (Hettema 2012, p. 42). According to the author, the rejection of the reduction of chemistry to physics leads to "[t]*he lazy conclusion that physics and chemistry occupy different* '*silos*' *or* '*paradigms*', *with no possibility of meaningful communication between the two*" (Hettema 2012, p. 413). And if this happens in the case of two areas as close as chemistry and physics, "*what hope is there for areas where the difficulties are more daunting, such as the medical sciences and biology*? [. . .] *What happens to the unity of science*?" (Hettema 2012, p. 413). Here the question is: does the meaningful communication between theories and disciplines inescapably require reduction? Must the unification of science necessarily rely on reductive links?

Certainly, the belief that reality is a harmonious whole and not an incoherent plurality has guided scientists throughout the history of science, and has lead them to the search for unification. Of course, the idea of unification acted as a powerful engine for scientific research and, for this reason, should not be abandoned. But although in most cases unification was conceived of in terms of reduction, this is not necessary. Our Kantian-rooted ontological pluralism does not give up the idea of unification, but retains it under a more flexible view that follows the perspective opened by Otto Neurath about this topic. According to this author, science is not oriented towards a single whole, but proceeds by means of local systematizations and, consequently, preserves a plural and always incomplete character. On this basis, Neurath favors an idea of unification based not on hierarchical links, but rather on a picture of science as an encyclopedia, where the connections between theories adopt very different, stronger or weaker, forms (Neurath 1935).

When intertheoretic relationships are studied in flesh-and-blood science, one can see the different kinds of resources needed to establish the links. In fact, the relations between theories are usually much more subtle and varied than what the traditional perspective supposes: they involve limits, coarse-graining, approximations and other mathematical techniques far more complex than the simple logical links involved in reduction. Moreover, they are not mere tools to which we turn in response to our perceptual or technological limitations.

This view about intertheoretic relationships should lead us to leave behind a traditional assumption about theories, according to which the entire nomological content of science is concentrated in laws, and any condition necessary to establish intertheoretic links represents an auxiliary and contingent aspect of a particular situation (see discussion in Wilson 1989). From the perspective of our ontological pluralism, the links between scientific theories do not play a role as secondary and accessory as usually assumed, but they represent a central and substantive part of the scientific knowledge. Intertheoretic relationships are *symmetric nomological links*: they work as "bridges" between theories, which can be "crossed" in the two directions. In other words, besides intratheoretic laws, there exist *intertheoretic laws* that do not impose relationships of priority or dependence between the corresponding ontologies; this kind of laws is what establishes a non-reductive and non-hierarchical articulation between theories.

The relationship between two theories and their corresponding ontologies is a single local nexus in a plural and complex structure. From the pluralist perspective, intertheoretic relations, when they can be established, do not lead necessarily to a hierarchy of levels, that is, to a "chain" where each "shackle" is connected only with the two immediately adjacent ones. On the contrary, the theories simultaneously accepted by the scientific community form a web, where each theory may be connected with more than two other theories, and through different links with each one of them. For instance, classical mechanics is related with classical statistical mechanics, with special relativity and with quantum mechanics by means of completely different links. As Gordon Belot and John Earman (1997, p. 162) make the point, "*we have a web of independent theories*, *each of which is thought to be empirically adequate within its own domain of applicability* [...] '*Web*' *rather than* '*hierarchy*' *here because theories often have more than one limit*: *for instance*, *special relativity is the curvature* $\rightarrow$ *0 limit of general relativity*, *while the curved spacetime formulation of Newtonian gravity is its* $c \rightarrow \infty$ *limit*." Scientific theories thus form a lattice structure on the basis of the nomological bridges connecting them. In this lattice, disciplinary boundaries become less important than usually conceived. This is precisely the case of the relationship between chemistry and physics: the domain traditionally considered proper to chemistry is organized as a lattice of theories with their intertheoretic links: those links, in certain cases, cross the traditional boundaries of the discipline to establish relations with theories belonging specifically to physics – without, nevertheless, diminishing the autonomy of the chemical theories and of their corresponding ontologies.

Summing up, the fears of authors such as Needham and Hettema are unfounded: the rejection of reduction does not undermine the unification of science. Far from leading to a disintegrated science, our Kantian-rooted pluralism incorporates a wide and meaningful articulation between scientific theories and disciplines. By recognizing the variety of intertheoretic relationships possible in science, this *non-reductive unification* transcends the conventional boundaries that separate – rather than bring closer – the different disciplines of science.

3.7 Conclusions

During the twentieth century, the development of the philosophy of science mostly proceeded by ignoring and even denying ontological matters. The problem of intertheoretic relationships did not escape the influence of this trend: it remained confined to semantic discussions about the way of obtaining terms and propositions of one theory from the terms and propositions of another theory considered more fundamental. It was only in the last decades that the interest in the ontological dimension of knowledge came back to the philosophy of science community. The Kantian-rooted ontological pluralism, with its attempt to rethink the links between scientific theories in the light of the problem of realism, intends to be a manifestation of this trend. From the pluralist perspective it is possible to face the question about the relations between incompatible ontologies, corresponding to theories simultaneously accepted by the scientific community, without confining some of them to an apparent or secondary position with respect to the supposedly "fundamental" realm. This approach offers us a diversified scientific reality, which unfolds in multiple ontologies, all of them equally objective and related with each other by non-hierarchical links.

Our ontological pluralism has been successfully applied in the resolution of some long-standing problems in the philosophy of physics (see discussion in Lombardi and Pérez Ransanz 2012, Second Part), such as the problem of determinism (Lombardi 2002) and the problem of irreversibility in classical statistical mechanics (Labarca and Lombardi 2007); it has also been suggested as an element for the solution of the problem of the classical limit of quantum mechanics (Castagnino and Lombardi 2004) and of the problem of irreversibility in quantum mechanics (Castagnino et al. 2005; Lombardi and Pérez Ransanz 2012, Chapter X). Of course, no argument or application can claim to serve as a definitive "proof" of a philosophical thesis. Therefore, even if we cannot persuade the critics of ontological pluralism, at least we have contributed to reinstalling the ontological discussion in the context of the philosophy of chemistry.

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Chapter 4
A Novel Approach to Emergence in Chemistry

Alexandru Manafu

4.1 Introduction

As noted by Kim (2006), "emergence" is a philosophical term of art. There is no unique or unified theory of emergence, and the meaning of the term varies from author to author. Many scientists with a philosophical bent love the term, as do some philosophers. But others complain that "emergence" is too vague and unhelpful. Despite this, there is a common set of features that many concepts of emergence share. Philosophers and scientists use the term "emergence" in relation to levels of reality. The picture often invoked is that of a layer cake: physics at the bottom, followed by chemistry, biology, psychology, etc., where each level is seen as harbouring novel entities,[1] properties, phenomena, which emerge from the interactions at the lower level.[2] This picture may be problematic, but if one accepts it, emergence is seen like a nice way to explain the relations between the levels.

When thinking about emergence in this way, two seemingly contradictory features become apparent. On the one hand, the emergents (be they entities, properties, phenomena, processes, laws, explanations, etc.) are seen as *dependent* on the lower level; on the other hand, emergents are seen as being *autonomous* from the lower level. These two features seem contradictory: how can one and the same set of things, properties, etc. be at the same time dependent and autonomous from another set of things, properties, etc.? I suspect this is one of the reasons

[1] Throughout this paper I am using the word "entity" to mean "concrete individual" or "object".

[2] The metaphor of the layer cake is due to Putnam and Oppenheim (1958), who adopted it to argue for a certain kind of reductionism.

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why emergence is sometimes seen as an incoherent position. But perhaps it need not be; perhaps there is a sense in which dependence and autonomy can coexist. A challenge that emergentists face, therefore, is to explain precisely how this can be. One way to do this is to conceive of dependence in terms of supervenience, and of autonomy in terms of the failure of reduction.[3] Thus, emergence can be seen as a version of nonreductive physicalism: *physicalism* because virtually all approaches to emergence recognize that at the basis, all there is is physical – the higher strata are seen as supervening on the physical; *nonreductive* because, for one reason or another, the higher levels do not reduce to the lower level.

Some authors go beyond this picture and see emergence as depending on downward causation (Hendry 2006). Others do not consider downward causation as a necessary condition for emergence (Batterman 2002). In this paper I will assume a fairly liberal concept of emergence – arguably, a theory which does not include downward causation can still be a theory of emergence if it talks about levels of reality which are dependent but autonomous from one another.

Developing theories of emergence can be useful to those who are concerned with the disciplinary autonomy of the special sciences. Since the emergents at one level are autonomous in relation to the lower level, it is natural to think that the science studying them is autonomous from the science studying the lower level. The autonomy of chemistry from physics continues to be debated. Some authors have attempted to ground the autonomy of chemistry in a philosophical position called internal realism (Lombardi and Labarca 2005). But others have argued that chemistry cannot be autonomous from physics if it reduces to it (Manafu 2013b). Thus, insofar as some kind of failure of reduction seems to be a central ingredient of emergence, emergence could perhaps account for the autonomy of chemistry.

Of course, whether chemistry is autonomous from physics depends on how one conceives of autonomy. Unfortunately, the notion of disciplinary autonomy has not been analyzed sufficiently in the philosophy of science. Many philosophers of science rely on an intuitive and implicit notion of autonomy.[4] One can distinguish between several types of autonomy. First, one can talk about historical autonomy. Historically, chemistry has been independent from physics. It has been claimed that chemistry had become a science "of great extent and certainty" long before we had any mechanistic insight into the internal make-up of the elements (Broad 1925). Broad argued that for a long time, progress in chemistry was possible without using

[3] A set of properties H supervenes on a set of properties L if and only if (i) any two objects x and y that have the same L properties will necessarily have the same H properties (though not necessarily viceversa), and (ii) any two objects z and w that differ in their H properties will also differ in their L properties (though not necessarily viceversa).

[4] Hendry (2012) is an exception, but he does not give many details. He writes: "A science is autonomous if its laws and explanations make no appeal to the laws or categories of other sciences." (Hendry 2012, p. 382).

any mechanistic assumptions. He concluded that the possibility of mechanistic explanation is not essential to the progress of chemistry.

> If then chemistry can be a scientific subject and can make steady progress without using the assumption that a mechanistic explanation of chemical phenomena is possible, it would presumably have made precisely the same progress if in fact no such explanation had been possible. (Broad 1925, p. 74)

While Broad is correct to point out that progress in chemistry happened long before modern mechanistic explanations of chemical phenomena became available, it is also true that the mechanistic insights that became available in the twentieth century have allowed for a great expansion of our chemical knowledge. They allowed us to better understand the chemical reactions that we knew about, and to design new reactions. They allowed us to synthesize new molecules, and even new elements, and to design and create new drugs and materials. In other words, chemistry would not have made precisely the same progress if quantum mechanics had not been discovered, although for a long time its own progress was independent from the progress of physics. Therefore, the autonomy of chemistry in relation to physics cannot be based solely on the notion of historical autonomy, which is also only partially defensible.

A second type of autonomy is methodological autonomy. In general, a chemistry lab looks very different from a physics lab and what goes on in a chemistry lab is different from what goes on in a physics lab. But one may respond to this by saying that while physics and chemistry differ with regard to their methodologies in general, the methods of some branches of chemistry are in fact physical in nature. For example, the bond length and angles of molecules are determined using various types of spectroscopy. Spectroscopy is used in physical and analytical chemistry to identify the composition of substances or to assess the concentration of a given chemical species; computational methods that make use of quantum mechanics are used to determine the structure of compounds. Although in general the methods of chemistry and physics are quite different, this does not demonstrate that chemistry is autonomous from physics. This is because the entities and properties that form the subject matter of chemistry could still be physical entities or properties, even if they are studied with non-physical (i.e., chemical) methods. Thus, what philosophers have in mind when they talk about the autonomy of chemistry in relation to physics is not captured solely by historical or methodological autonomy.

A stronger notion of autonomy can be discussed – the so-called *ontological* autonomy of chemistry. Indeed, this stronger notion of autonomy is the one which presents the most philosophical interest. But what does it amount to? I make the following proposal: a discipline is ontologically autonomous from another if the ontology of the first is distinct from the ontology of the second. To be informative, this proposal must specify what it is meant by "ontology". Luckily, we have a pretty decent understanding of what an ontology is. Arguably, an ontology must

include: entities, processes, phenomena, properties, laws. To this list one may add explanations, if they are viewed ontically, not just epistemically.[5] If all these turn out to be physical entities, properties, etc. in disguise, then it is pretty clear that chemistry cannot be autonomous from physics. For chemistry to be ontologically autonomous from physics, chemistry must talk about its own entities, processes, properties, laws. These must be *sui generis*. In other words, they must be *chemical* properties, laws, etc. in their own right, not just species of physical properties, laws, etc.

The ontological autonomy of chemistry is tied with the failure of (at least some versions of) reductionism. Indeed, if all chemical laws are obtainable from quantum-mechanical laws, then how could the belief in the autonomy of this discipline be maintained? Since emergence makes possible the existence of sui generis chemical properties, laws, and explanations, it is natural to think that emergence can justify the ontological autonomy of chemistry.

Here is the plan of this paper. The next section summarizes the current state of the debate regarding ontological emergence in chemistry. The current approaches to ontological emergence in chemistry have been met with scepticism, and some have argued that the appropriate attitude regarding ontological emergence in chemistry is agnosticism (Scerri 2012). In the third section I offer a novel approach to emergence in chemistry; the approach is in some sense weaker than the existing approaches, but I argue that it can justify the ontological autonomy of chemistry. In the fourth section I discuss a couple of objections to this approach and speculate a bit on what it entails about the nature of chemistry as a science and about the appropriate model of the relationship between the special sciences. The concluding section summarizes the main points.

4.2 The Present State of the Debate About Emergence in Chemistry

There are several contemporary approaches to emergence which are applicable to chemistry, including Humphreys (1996, 1997a, b), Luisi (2002), Hendry (2003, 2006, 2010a, b), Llored (2012).[6] In this section I will focus only on some accounts which claim to be ontological (as opposed to merely epistemic) and which apply explicitly to chemistry. More precisely, I will be focusing on the account of emergence recently defended by Hendry.

[5] An ontology includes objects, phenomena, as well as relations between them. If one includes explanations, then they could be regarded as objective relations between laws and phenomena. The idea that explanations could be seen ontically does not sound as implausible if one thinks that it makes sense to say that for a certain phenomenon an explanation exists but it may never be found.

[6] For a comprehensive review see Manafu (2013a).

To understand the present state of the debate it is useful to start with Broad, for whom chemistry "seems to offer the most plausible example of emergent behaviour" (Broad 1925, p. 65). It is useful to do so because Hendry's account is relying on Broad's. Broad uses an older distinction made by Mill (1882) between purely mechanical behaviour and chemical behaviour. For Broad, a system is emergent if its properties cannot be predicted from a knowledge of the properties of its constituents taken separately or in other wholes, including knowledge of their inter-relations. According to Broad, the only way to learn about the chemical properties of a chemical compound is empirically, by studying samples of that compound. If we start with knowledge of the components and the relations between the components and we try to determine the properties of the compound, then – if chemical compounds are truly emergent – we are bound to fail. Our failure is not due to some mysterious chemical spirits similar to the élan vital in biology; for Broad, the natural kinds that are the subject matter of chemistry are wholly composed of the kinds that are the subject matter of physics. Nor is it necessarily due to the lack of precise knowledge of the initial conditions or computational power. Rather, the problem is more fundamental – the "unique and ultimate" character of the laws of chemistry (Broad 1925, p. 65). Such laws, which connect the properties of chemical compounds with the properties of their components are called by Broad trans-ordinal laws. According to Broad, our failure is due either to (i) the existence of innumerable "latent" properties in each element, each of which is manifested only in certain conditions, or (ii) to the lack of any general principle of composition, such as the parallelogram law in dynamics, by which the behaviour of any chemical compound could be deduced from its structure and from the behaviour of each of its elements in isolation (Broad 1925, pp. 66–67).

McLaughlin interpreted Broad (or more generally British emergentism) as holding the view that an emergent whole possesses force-generating properties of a sort not possessed by any of its parts (McLaughlin 2008, p. 41). On this view, when particles are arranged in certain select configurations, new, unanticipated forces arise. McLaughlin called these forces *configurational*.[7] In chemistry, configurational forces are supposed to be sui generis chemical forces characterizing the compounds, irreducible to physical forces characterizing the components. They are supposed to be capable of downward causation – the ability to influence the basal conditions from which they arise (i.e., the underlying dynamics). It is perhaps natural to think that on Broad's view these forces may be responsible for the failure of compositionality and the emergent behaviour of chemicals, including chemical affinity. McLaughlin contrasted configurational forces with resultant forces, i.e., non-emergent forces which are generated by other forces, not by configurations of particles. "Emergence", therefore, has been contrasted with "resultance".

[7] Although Broad does not use this term, McLaughlin (2008) interprets Broad in this way. According to McLaughlin, "it is clear that he [i.e., Broad] maintains that certain structures of chemical compounds can influence motion in fundamental ways" (McLaughlin 2008, p. 47).

McLaughlin finds the kind of emergentism espoused by Broad "enormously implausible". According to McLaughlin, the fall of British emergentism was not caused by some philosophical difficulties, but by advances in science:

> [Q]uantum mechanical explanations of chemical bonding in terms of the electro-magnetic force [. . .] render the doctrines of configurational chemical [. . .] forces enormously implausible. (McLaughlin 2008, p. 49)

McLaughlin's view has been widely embraced by philosophers. It would not be too exaggerated to say that it has become the orthodoxy amongst contemporary philosophers. But this orthodoxy has been challenged by Scerri (2012) who questioned the idea that progresses in theoretical physical chemistry have dealt a death blow to Broadian emergence. Scerri argues that today's theories of bonding still do not allow us to predict in advance the properties of compounds based on the properties of the components. Indeed, in all but the simplest cases, the theoretical and computational difficulties are enormous. But Scerri does not believe that this warrants one to draw the conclusion that emergence as conceived by Broad is a genuine phenomenon. Rather, Scerri distinguishes between what he calls "apparent emergence" (i.e., epistemic emergence, which might occur because of the limitations of our current theories) and "ontological emergence" (i.e., a deeper kind of emergence, which might occur because of the reasons presented by Broad). It is not hard to argue that chemistry does exhibit some sort of epistemic emergence, but according to Scerri it is an open question whether it exhibits ontological emergence as well.

Broad's account of emergence has inspired a prominent contemporary account of ontological emergence in chemistry, due to Hendry (2003, 2006, 2010a, b, 2012). Instead of employing configurational forces, Hendry employs "configurational Hamiltonians" – non-resultant Hamiltonians governing the behaviour of the molecule. Hendry gives as an example the CO_2 molecule. One can view the parts of this molecule as quantum mechanical harmonic oscillators and rigid rotators. But one can do this only after one assumes the linear structure of CO_2. Where does this assumed molecular structure come from? Hendry argues that rather than deriving this structure using resultant Hamiltonians, the linear structure of CO_2 is put in "by hand". For Hendry, this is tantamount to assuming "configurational Hamiltonians". Since the overall molecular structure constrains the motions of the parts of the molecule, this would count as an example of downward causation.

Now, the reductionist may agree that the molecule as a whole constrains the motion of its parts. But he may still disagree that this is a genuine case of downward causation; the reductionist may say that the powers of the molecule to constrain the motion of its parts come ultimately from the parts themselves, and their interrelations. We use the configurational Hamiltonians, the reductionist may argue, just because the real (resultant) Hamiltonians are just too hard to obtain. Thus, the configurational Hamiltonians are just approximations to the real (resultant) Hamiltonians, and their adoption does not make much of a difference. But Hendry argues this answer won't work. Hendry starts by pointing out that in the calculation of the wavefunction of the molecule one makes use of the Born-Oppenheimer approximation, which allows the molecular wavefunction to be broken into its electronic and nuclear components, and in which the nuclei are considered

"clamped". But following Woolley and Sutcliffe (1977), Hendry argues that in the process of applying the Born-Oppenheimer approximation, the symmetry properties of the molecular wavefunction are removed (Hendry 2010a, b). The idea here is that quantum mechanics cannot recover the structure (and the lower symmetry) of real molecules. For example, in the case of isomers, quantum mechanics cannot distinguish between two different molecules, for it assigns the same wavefunction to two distinct molecular structures – a wavefunction which is in fact a superposition of the wavefunctions corresponding to the two definite molecular structures (and has thus a higher symmetry). Hendry suggests that just as the measurement problem in quantum mechanics cannot be solved by a "superposition approximation" (i.e., simply discarding the part of the wavefunction that does not correspond to what is observed), it is just as much a mistake to invoke the Born-Oppenheimer approximation to argue that the structure of molecules is determined by resultant, albeit hard to obtain Hamiltonians.

In reply to Hendry's arguments, Scerri (2012) has pointed out that the lower symmetry of the molecules can be accounted for by their quantum-mechanical interaction with the environment (decoherence). Molecules are never in isolation; they are always surrounded by other molecules, to which they interact. Consequently, the wavefunction of a given molecule will not be for a long time in a superposition of states corresponding to two different molecular structures. The idea here is that pretty fast, the superposition will collapse and the molecule will assume the observed structure. Scerri claims that "taking account of quantum decoherence allows one to tame the effect of entanglement and appears to alleviate the concern that ontological entities such as molecules with particular structures might not exist in their own right" (Scerri 2012, p. 20).

The appeal to decoherence is an interesting move, but it is not without its problems. First, it should be mentioned that decoherence does not solve the problem of definite outcomes, which together with the problem of the preferred basis forms the so-called measurement problem in the foundations of quantum mechanics (Adler 2003; Zeh 2003). Decoherence just passes the entanglement on to the environment. In fact, decoherence exacerbates the measurement problem. Scerri recognizes that decoherence does not allow one to predict any particular outcomes. But he claims that this concern can be addressed by assuming that the collapse is ubiquitous, and it happens even in the absence of observers. He claims that this intuition is supported by the fact that the classical world is populated by definite outcomes (i.e., definite outcomes are not just an effect of conscious observers). But these remarks essentially amount to taking a stand on the interpretation of quantum mechanics; of course, they do not by themselves amount to an interpretation of quantum mechanics, but they favour a set of interpretations over others. So it looks like that the debate about configurational Hamiltonians and molecular structure has become entangled with the problem of interpreting quantum mechanics. Thus, it seems that to elucidate the hard problem of emergence in chemistry one needs to elucidate a perhaps even harder problem. Since there is the risk that this debate could degenerate into a debate about the proper interpretation of quantum mechanics or even turn into a stalemate, perhaps it is worth considering a different approach to emergence in chemistry.

Insofar as Hendry's theory of emergence focuses on entities, it is at odds not only with reductionism, but also with the causal closure or completeness of physics – the thesis that "all physical events are determined (or have their chances determined) entirely by prior physical events according to physical laws" (Papineau 1990, p. 67). This is because on Hendry's view, molecules are capable of downward causation. So if the theory of emergence advocated by Hendry is true, the set of physical causes must be supplemented with sui generis chemical causes – molecules exerting downward causation on their parts.

The rejection of the causal closure of physics entailed by the kind of ontological emergence advocated by Broad and Hendry may be problematic. Some philosophers argued that the causal closure of physics is supported by inductive arguments based on the history of science (Papineau 2002, see Appendix) or on conservation laws (Vicente 2006).[8] One worry is that in a world in which all basic forces are physical and the conservation of energy is respected, *sui generis* non-physical forces (whatever this might mean) of the kind required to break the causal closure of physics could not arise. Maybe this objection can be responded to, and maybe the causal closure of physics is just another philosophical preconception of the naturalistic-minded philosopher. Or maybe not. Regardless, it seems to me that it would be preferable if the ontological autonomy of chemistry did not depend on a theory of emergence which is committed to the falsity of the causal closure of physics. This is another reason why it may be fruitful to approach emergence in chemistry differently.

Scerri's view on the current state of affairs regarding emergence in chemistry is that just as McLaughlin has failed to rule out emergence and downward causation, so Hendry has failed to make a case in their favour. Scerri believes that the proper attitude to adopt towards emergence and downward causation in chemistry is agnosticism. Given the points I made earlier (about how the debate over the kind of emergence defended by Hendry might require one to take a stand on the interpretation of quantum mechanics, and about how the rejection of the causal closure of physics that it entails might be at odds with the principle of the conservation of energy), but also given what is at stake (namely the disciplinary autonomy of chemistry), I think it is worth investigating alternate routes to emergence. The rest of this paper sketches such a proposal.

4.3 A Novel Approach: Functional Emergence

Before sketching the contours of a new approach to emergence in chemistry it would be useful to state why such an account is desirable and what we want from it. As mentioned in the introduction, developing accounts of emergence in chemistry is important because emergence can help us defend the ontological autonomy

[8] For a different view, see Gibb (2010).

of chemistry. The question that I think needs to be taken seriously is this: if the entities that chemistry talks about are composed of nothing but the entities that quantum mechanics talks about, why do we have chemistry and not just applied quantum mechanics? Are there any good reasons for upholding the ontological autonomy of chemistry, as opposed to just a merely epistemic, methodological or historical autonomy? If the kind of stuff chemistry talks about consists of the kind of stuff that quantum mechanics talks about, what justifies belief in chemical properties, or that in chemical laws or explanations? Are there even *chemical* properties, laws, and explanations, as opposed to just complex quantum-mechanical properties, laws, and explanations? Does chemistry latch onto genuine features of the world, which inhabit a distinct ontological level? Or rather the chemical properties and laws are just useful instruments for predicting and explaining, but ultimately with no claim to the fundamental truths about nature, which remain microphysical? If chemistry is emergent, then these questions may find satisfactory answers. If one can show that there really are *chemical* entities, properties, laws and explanations, then the ontological autonomy of chemistry can be secured.

So far, the philosophical efforts towards a theory of ontological emergence in chemistry focused on the emergence of entities. For Broad, what was emergent was chemical compounds; for Hendry, what is emergent is molecules (molecular structure). But an ontology contains more than just entities; it also contains processes, properties, phenomena, laws, and on some understandings of ontology, even explanations. All these are just as legitimate elements of an ontology as entities. The approach I am proposing focuses not on entities, but on properties and laws, which can be used in *sui generis* chemical explanations. It starts from the observation that many chemical properties are defined not in terms of their constitutive microphysical structure, but functionally, in terms of their efficient roles. In particular, many chemical properties are defined by their behaviour in relation to other chemical properties, in the context of chemical reactions. The idea that a thing is defined by what it does and not by what it consists of was first advocated by Alan Turing, in the foundations of computer science and artificial intelligence (Turing 1950). Turing thought about it via an analogy with the mathematical concept of a function (1950, p. 439). Turing's idea was quickly adopted in the philosophy of mind, where it served as a basis for an alternative theory of mind, different from both the identity theory and behaviourism (Putnam 1975a, b; Fodor 1974). The theses of functionalism and multiple realizability have also inspired anti-reductionist arguments in the philosophy of biology (Kitcher 1984, 1999; Kincaid 1990). But chemistry is, I believe, the ideal domain where this sort of anti-reductionist argument can be made. The fact that chemical properties can be intersubjectively scrutinized, that they are amenable to measurement, experiment and to a quantitative understanding to a greater extent than those in the other special sciences makes chemistry one of the best case studies (see also Scerri and McIntyre 1997, p. 227; Humphreys 1997b). Chemistry is the discipline that is in some sense closest to physics, and therefore it is the first domain outside physics itself where we can observe functional properties and irreducibility/emergence, if these truly exist.

The approach to emergence I'm proposing starts from the observation that many chemical properties are defined not in terms of their constitutive microphysical structure, but functionally, in terms of their efficient roles. So far, philosophers of

chemistry have not given appropriate consideration to this idea. For example, the volume which was published as a result of the 3rd Erlenmeyer Colloquy for the Philosophy of Chemistry, titled "The Autonomy of Chemistry" does not even mention chemical functional properties, despite the broad consensus and shared anti-reductionist attitudes among the participants (Janich and Psarros 1998). In fact, the idea of multiple realizability (which is often associated with functionalism) has been regarded with distrust in the philosophy of chemistry, being labelled as "wishful thinking" (Scerri 2000). Yet, multiply realizable properties feature prominently in the discussions about the limits of reductionism in philosophy of mind, philosophy of biology, and philosophy of physics (Batterman 2000, 2002). I think chemistry makes no exception; on the contrary, I think chemistry provides us with some of the best examples of functional, multiply realized properties.

Consider the property of being an acid. On the Arrhenius definition, acids are defined as those substances which, when dissolved in water, increase the concentration of hydrogen ions in the solution. On the Brønsted-Lowry definition, an acid is any compound that can donate one or more protons to other chemical species in chemical reactions. And on the Lewis definition, acids are those compounds that accept a pair of electrons from another compound in a chemical reaction. All these definitions are functional, i.e., they pick out acids not by referring to their microphysical structure, but by referring to their behaviour in relation to other chemical substances. Compare the property of being an acid with the property of being an alcohol. Alcohols are those molecules that have a hydroxyl group bound to a saturated carbon atom. This microstructural commonality can be invoked when explaining the chemical properties of alcohols. In a certain sense of the term "reduction", the property of being an alcohol reduces (i.e., is identical) to the property of being a microphysical system containing a hydroxyl group bound to a saturated carbon – all alcohols and only alcohols have this microstructural property. But the property of being an acid (or, more accurately, acidity in general) does not "reduce" in a similar manner to any given microstructural property. Of course, one may accept that any given instance of an acid (or acidic behaviour) is identical with a given instance of a physical property or process – token reductionism may hold. But acidity as such (as a property type) cannot be identified to any given microstructural property – type reductionism fails. Acidity is first and foremost a behaviour, which can be realized by many systems of electrons and nuclei. In philosophical lingo, the property of being an acid is said to be *multiply realized*. Because of this, it is not discernible at the lower level as a microstructural property. It "emerges" out of the microphysics, and becomes visible only in the context of a chemical reaction, as a pattern of chemical behaviour.

Acidity may not be the only functional property in chemistry: arguably, the property of being a base, a reductant, an oxidant may also be functional. To these, one may add the property of being a metal. More than 70 % of existing chemical elements are metals; at standard conditions of temperature and pressure, 91 elements out of 117 are considered metals. Twelve out of 18 groups in the periodic table are occupied exclusively by metals – alkali elements, alkaline earth elements, lanthanides, actinides, and the transition elements, are all metals. Some elements in group 13 to group 16 are metals too. As one can expect, the microstructural description for all these atoms will look disunified. Finding a microstructural

feature that is shared by all metal atoms and only by them is highly implausible. Despite the fact that their microstructural descriptions are wildly heterogeneous, metals have interesting chemical properties in common: their atoms readily lose electrons to form positive ions; they form metallic bonds with other metal atoms and ionic bonds with nonmetal atoms. Since the property of being a metal is not characterized by a shared microstructure, but by what the entities instantiating the property can do, this property is also functional.

Functional properties in chemistry are not only multiply *realized* (in the sense of there being many systems composed of electrons and nuclei that can carry out the specified role), but they are also multiply *realizable* – the list of systems composed of electrons and nuclei that can carry out the specified role is open ended. Chemistry is in the business of synthesising new substances. Although synthetic elements have also been created, most of the synthetic substances are compounds. For any functionally defined chemical property like acidity, chemists can come up with new compounds which can carry out that behaviour.

If there are functional, multiply realizable properties in chemistry, then this means that certain notions of reductionism cannot be maintained. I have already mentioned type reductionism. Type reductionism (or, as Fodor called it, "type physicalism") is the idea that every property mentioned in the laws of any science is a physical property. If type reductionism were true, there would be a one-to-one correspondence between chemical properties and microstructural properties. The kinds that chemistry talks about would be shown to be identical to, or at least coextensive with, physical kinds. For some chemical properties (like the property of being an alcohol) this is in fact true – as stated, there is a one-to-one correspondence between alcohols and microphysical systems containing a hydroxyl group bound to a saturated carbon atom. But for other chemical properties (like the property of being an acid) it is not. This suggests that properties like acidity are not physical properties in disguise; they are *sui generis* chemical properties, i.e., chemical properties in their own right. Acidity is made possible by physical processes at the lower level, and any instance of acidic behaviour (i.e., any particular reaction) may be identical to (or coextensive with) a specific physical process at the lower level. But acidity as a property *type* is not identical to (or coextensive with) any microstructural physical property. It emerges as a property only when one zooms out of microphysics and starts looking not at microphysical structures, but at their behaviours.

The existence of functional properties in chemistry also impacts reductionism about chemical laws. On Nagel's concept of reduction (1961), chemistry would reduce to physics if one could derive all the laws of chemistry from the laws of physics together with bridge laws connecting the terms in the vocabularies of the two sciences.[9] The philosophical literature on Nagelian reduction has long debated

[9] In this context, by "chemical laws" I do not mean exceptionless and timeless universal truths, of the kind that occur in fundamental physics (or maybe not even there). Rather, I mean the kind of regularities chemists use on a daily basis, and which chemistry students find circled in chemistry textbooks. For example, the statement that "Acids in reaction with metals generate hydrogen gas" would count as a chemical law. If one does not accept this charitable reading of what a law should mean, then the Nagelian reduction of chemistry to physics cannot even begin to be discussed.

the implications of multiple realizability for bridge laws. If one conceives of bridge laws as a posteriori identity statements, then bridge laws must be biconditionals linking kinds. That is, they must connect a chemical kind with exactly one micro-physical kind.[10] Multiple realizability prevents this one-to-one connection.[11] But even if the reductionist retreats to a one-to-many connection between a chemical property and a heterogeneous set of physical properties, it is still unclear that the desiderata of Nagelian reduction can be met. As mentioned, the reduction of chemistry requires the derivation of chemical laws from physical laws. But it is questionable that the relationship between the physical realizers of the functional properties which figure in some chemical laws would have any nomic character. Consider the chemical law that acids in reaction with metals generate a metal salt and hydrogen. The number of compounds rendering this chemical law true is vast. Take the following two examples (in aqueous solution):

$$H_2SO_4 + Fe \rightarrow FeSO_4 + H_2$$
$$2HCl + Zn \rightarrow ZnCl_2 + H_2$$

Now, to paraphrase Fodor (1974), one may say that while it is a law that sulfuric acid in reaction with iron produces iron sulfate and hydrogen, and it is a law that hydrogen chloride in reaction with zinc produces zinc dichloride and hydrogen, it is not a *law* that either sulfuric acid or hydrogen chloride in reaction with either iron or zinc produces either iron sulfate and hydrogen, or zinc dichloride and hydrogen. This last statement is too gerrymandered to have any nomic character. Nonetheless, the more general claim, asserting that acids in reactions with metals produce a metal salt and hydrogen, is a law. Even if the two statements above expressing the reactions can be construed as stating laws of physics (which is in itself problematic), one could not use them to deduce the chemical *law* that acids in reaction with metals generate a metal salt and hydrogen. Since the nomic character of this statement (and of similar statements relating functional properties) cannot be recovered from the reduction base, such statements – if laws at all – must be regarded as *sui generis* chemical laws.

The functional, multiply realizable chemical properties may occur in higher level chemical explanations. Q: "Why did the marble antefixes on the roof the Philadelphia Merchants' Exchange lose their detail?" A: "Because of the acid rain." I take it that this is a perfectly satisfactory explanation. The answer successfully selects one of the contrast classes (chemical) and eliminates the others (mechanical, temperature variations, etc.). Admittedly, the explanation is not specific; it does not mention the precise composition of the acid rain, and it leaves out the specific chemical reactions. But this is not necessarily a defect of the explanation; in fact, it

[10] I am assuming a strong connection between kinds and properties.

[11] Of course, one may reply by saying that bridge laws need not be biconditionals. But there are many problems with this move, and this is not the place to discuss them. I will just mention Fodor who writes that if the relation in the bridge law "is interpreted as any relation other than identity, the truth of reductivism will only guaranty the truth of a weak version of physicalism" (1974, p. 99).

can be a virtue. By not going into the details, the explanation is *unified*: it sees various compounds as instances of a single kind of substance, namely acid. Since the explanation is insensitive to the particular compounds responsible for the acidic properties of the rain, it is *robust*: it remains valid despite variations in the composition of the acid rain that may occur from year to year. Also, the explanation has a *broad explanatory range*: it can account for the loss of detail in the marble antefixes on buildings situated in different geographical locations, where the acid rain has a different chemical composition. Since it features a sui generis *chemical* property, the explanation above may be called a sui generis *chemical* explanation. In contrast with the explanations mentioning the particular reactions (which perhaps could be seen by a ruthless reductionist as physical explanations), the explanation invoking the acidity of the rain is robust, unified, and has a broad explanatory range. But this happens only because it is a higher level explanation, i.e., an explanation which employs a higher level concept.

If chemical properties, laws and explanations are not identical or coextensive with physical properties, laws and explanations, then they should be treated as *sui generis*. The existence of sui generis chemical properties, laws and explanations supports the idea that chemistry is ontologically autonomous from physics, which is one of the two defining characteristics of emergence. The other characteristic of emergence, namely dependence, is also satisfied by the account I'm proposing. The functional chemical properties like acidity are made possible by the physical processes involving systems of electrons and nuclei. The kind of emergence I'm proposing has no problems embracing *supervenience physicalism* – the idea that any physical duplicate of our world is a duplicate of our world simpliciter. I take the following to be true: (i) if the microphysical level were to disappear, the chemical level would disappear as well; (ii) any change at the chemical level must involve a change at the microphysical level; (iii) any microphysical duplicate of our world will be a chemical duplicate.

Since the view I'm proposing meets both characteristics of emergence, and is made possible by the existence of functional properties, I will call it *functional emergence*. The use of the term "emergence" is appropriate because the existence of functional properties in chemistry supports the layered view of the world characteristic of emergentism. The sui generis chemical properties, laws and explanations function at a higher level than the physical properties, laws and explanations; they depend on the physical level, but they do not reduce to it.

I take it that supervenience physicalism is an uncontroversial thesis, which can be shared by reductionists and emergentists alike. But, as mentioned earlier, not all versions of emergence share a deeper physicalist commitment, namely the completeness of physics. For example, those versions of emergence which are committed to the emergence of entities (e.g., Broad's or Hendry's) will conflict with the thesis that all physical events are determined (or have their chances determined) entirely by prior physical events according to physical laws. For if there are sui generis chemical entities which are capable of causing physical events (via downward or horizontal causation) then the causes of those events won't be strictly speaking physical; they will be *chemical*. But functional emergence does not take this step. On the view that I'm proposing, entities may be wholly resultant.

Functional emergence need not be committed to the emergence of entities, or to their ability to exert downward causation; it is committed solely to the emergence of properties, laws, and explanations. As a result, there need not be any conflict with the completeness of physics; functional emergence and the completeness of physics can peacefully coexist.

4.4 Two Objections

There are several problems with the view that I'm sketching, but I will only discuss two of them. First, one may object to calling the account of emergence I'm proposing *ontological*. Since on this account entities do not count as emergent, why claim that functional emergence is a kind of ontological emergence? After all, if all chemical entities are composed of nothing else except microphysical entities, doesn't this mean that the ontology of chemistry reduces to, or is a subset of, the ontology of physics?

The problem with the argument above is that it construes ontology in a restricted way, as referring exclusively to entities (i.e., individuals). Ontology is concerned not only with entities, but also with properties, laws, and on some accounts, explanations. If one distinguishes between a property and its instances, as one should, the fact that every instance of a chemical property is composed of nothing else except instances of microphysical properties does not mean that all chemical properties are in fact microphysical properties in disguise.[12] Similarly, it would be a mistake to think that if all events are governed by physical laws, then all laws must be physical. Although the entities that chemistry talks about may be composed of nothing else except microphysical entities, this leaves open the possibility of sui generis chemical *properties* and *laws*. But if that is the case, there is a sense in which one can still talk about the ontological autonomy of chemistry. This result contrasts with the view advocated by McIntyre, who argued that the ontological interpretation of the concept of emergence should nearly always be eschewed in favour of an epistemological interpretation (McIntyre 2007).

It must be admitted, however, that this ontological autonomy is not radical: if the entities that microphysics talks about were to vanish, there would be nothing left; consequently, there would be no chemical properties, no laws relating these properties, and no explanations employing those laws and properties; although the ontology of chemistry is autonomous from the ontology of physics, it relies upon it.

The second problem is that not all chemical properties are defined functionally. What does this situation tell us with respect to the nature of chemistry as a science, and its autonomy from physics? In my view, this situation reflects the status of chemistry as "the first" of the special sciences. Some chemical properties (like the property of being an alcohol) can be reductively identified with microphysical

[12] For the distinction between a property and its instances see Swoyer and Orilia (2011).

properties. But others (like being an acid), are defined functionally, and they will not be reducible to any particular physical properties. This depicts an image of chemistry as a "mixed" science – a science that is close enough to physics so that some of the properties it talks about are microphysical properties, but also a science that begins to emancipate itself from the base, and deals with genuinely new properties. The "mixed" character of chemistry qualifies the thesis that chemistry is ontologically autonomous from physics, and perhaps it weakens it to some extent. Nonetheless, it would be wrong to conclude that the mixed character of chemistry makes the ontology of this discipline as a whole a sub-domain of the ontology of physics. Since the sui generis properties and regularities that chemistry talks about are sufficiently numerous and pervasive, the ontological autonomy of chemistry can be preserved.

This image of chemistry as a "mixed science" offers only a partial support to the classical layer cake model of science that has been assumed by many reductionists, anti-reductionists and emergentists alike. The chemical properties and regularities are always susceptible of disruptions "from below". In other words, chemical properties and regularities can always be affected by physical or microphysical factors. A clear example is the influence of temperature on chemical reactions, but numerous other examples could be found. Physical factors such as electromagnetic fields, pressure, even gravity may interfere with chemical properties and laws, no matter how sui generis these are. Thus, although chemistry has its own ontology which is distinct from that of physics, is not "insulated" from physics. To express this in the terms of the layer cake metaphor, chemistry is not a perfectly distinct layer that lays flat on top of the physical layer. Instead of the layer cake model, perhaps a better model could be suggested, one which captures more accurately the relationships between the various sciences. For the lack of a better metaphor, this could be called the "Easter bread" model. In the "Easter bread" model, the sciences are not arranged neatly in distinct layers, with physics at the base and then followed by chemistry, biology, psychology, etc.; rather, they interweave and penetrate each other globally, although locally they typically retain their distinctness.

4.5 Conclusion

In this paper I attempted to outline a novel approach to emergence in chemistry. The motivation for this was twofold: on the one hand, emergence is a way to secure the ontological autonomy of chemistry from physics; on the other, the most prominent approaches to ontological emergence in chemistry have been met with scepticism. The account I proposed differs from the most prominent existing accounts in several ways. What is emergent on my account is not entities, but properties, laws and explanations. Although the account I'm proposing may be new to chemistry, it is not new to philosophy (though the phrase "functional emergence" as I used it here may be). Functional properties which are multiply realizable have long been associated with a philosophical position known as nonreductive

physicalism. Like emergence, nonreductive physicalism attempts to reconcile physicalism with the idea that the special sciences are not reducible to physics.

The account I proposed here amounts to little more than a sketch. There are still many important questions to be answered, and many of its aspects need to be elaborated in more detail. The arguments I used here need to be improved and expanded; many imperfections need to be ironed out; in one word, a lot of work remains to be done. But the broad outlines I sketched here are, I think, essentially correct.

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Chapter 5
The Methodological Pluralism of Chemistry and Its Philosophical Implications

Joachim Schummer

5.1 Introduction

Much of today's mainstream philosophy of science is still built on the normative assumption that science should develop one comprehensive and logically consistent image of the world. Because there is only one world, science must strive for its perfect image to be pursued by the best method, the primary rule of which requires that contradictory views should be avoided or eliminated. For philosophers, methodology thus came to be known as the art of evaluating competing images or theories, with the implication that in the end one such method could ideally lead to one perfect theory (methodological monism). In contrast, scientists consider methodology the art of raising and solving epistemic issues, from formulating interesting research questions, to planning and conducting experimental research and discussing their results. As diverse as the research methods are, as diverse are at least the results.

Methodological pluralism, as understood in this paper, comprises both the diversities of research approaches and the resulting views on the world. The case of chemistry is particularly apt to illustrate pluralism of various kinds, such that this paper only adds to a longer list of previous work (e.g. Bachelard 1932; Hoffmann and Laszlo 1991; Chang 2012). As pluralism slowly gains acceptance in mainstream philosophy (e.g. Kellert et al. 2006), chemistry is expected to attract more attention, because there are valuable philosophical lessons to learn from it.

In the following I will first point out the pluralist constitution of science in general and of chemistry in particular and then argue that it is inevitable for epistemological reasons (Sects. 5.1, 5.2, and 5.3). Once methodological pluralism

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is accepted, many mainstream philosophical debates that are based on monism become futile, of which I discuss "laws of nature", "reductionism", and "scientific realism" (Sects. 5.4, 5.5, and 5.6). That shifts philosophical debates to more useful issues, such as the methodology of models, improving interdisciplinarity, and institutionalized forms of philosophical realism. The conclusion summarizes these and other advantages of pluralism as the better way of doing and understanding science.

5.2 The Pluralist Constitution of Science

Science as a whole is a pluralist enterprise. At least since the nineteenth-century, it regularly splits into different disciplines, subdisciplines, and research fields. Growing on average at an annual rate of 4–5 % over several centuries, the numbers of papers, scientists, fields, etc. roughly double every 15 years (Price 1961). As a human endeavor science depends on the limited intellectual and social capacities of its members. If you want to keep up with the latest work, you can read at most a few hundred or thousand papers a year. However, in chemistry alone more than one million publications appear annually, covered by Chemical Abstracts. If you want to find agreements with your colleagues on what are important research questions, what needs to be done or improved in the future, or what should be standards of sound argumentation and experimentation, you can personally discuss all that with hardly more than a few hundred colleagues despite modern communication technology. As long as science grows and reading and discussing are prerequisites of doing research, the fragmentation of science is an unavoidable process.

On the one hand, the ongoing splitting follows a division of labor. Different subdisciplines study different subject matter and develop their own research questions as well as their corresponding conceptual apparatus and methods. Sometimes they focus on entirely different objects, as once did organic and inorganic chemistry, such that under the common umbrella of general chemistry the fields, neatly separated, could complement each other without competition or disagreement – before the rise of organometallic, metalorganic, bioinorganic, biometalorganic etc. chemistry. Or, as in kinetics and thermodynamics, they study the same objects, i.e. chemical reactions, from different but complementary perspectives. On the other hand, a field can also split up because there is disagreement on the conceptual framework, such that one group prefers a new frame whereas the other sticks to the old one. A case in point is the mid-twentieth-century separation of molecular biology from biochemistry. While the latter continued the study of chemical processes in living organisms in terms of reaction pathways, i.e. the transformation and migration of matter, the former built its disciplinary identity on the conceptual framework of information transfer (Fox Keller 2000). Given the rapid growth and unavoidable fragmentation of science, it is likely that most cases of conceptual disagreement and conflict follow this kind of pattern. That is in strong contrast to the winner/looser stories of Popper, Kuhn and the like, who assumed that science would always (have to) pursue unity by

eliminating competitors. While the received philosophies of science have presupposed strict conceptual unity in their own pictures, including Kuhn's notion that temporary crises turn into new types of "normal science", the actual science is the result of an ongoing process of fragmentation, because that has always been the obvious way of solving conceptual disagreement under the pressure of growth.

How much the received philosophy has left science in the dark comes to the fore in the manifold obstacles faced by interdisciplinary research. What once split into parts frequently out of historically contingent reasons, is later required to collaborate on cross-disciplinary issues that are increasingly posed from science policy. The barriers of cross-disciplinary communication are enormous (Schummer 2008). They do not only include differences in knowledge and expertise, which a smart division of labor management could possibly fix. In addition, the same terms, like "molecules", frequently have different meanings in the disciplines, depending on the theoretical context they are embedded in, which easily results in misunderstanding and confusion. Moreover, disciplines differ in the way they approach a problem, what they consider a satisfying answer or sound argument, and, more generally, what counts as important research questions worth pursuing. Thus, besides differences in knowledge and linguistic meaning, disciplines have distinctive ideas about methods and epistemic values that have steadily been developed through internal discussion.

One cannot solve those serious problems by claiming that the world consists of a certain set of building blocks to be investigated by a universal scientific method, if the building blocks and methods happened to be just from a single discipline. It does not help either to hope that all problems will disappear in the future by a not yet found universal Theory of Everything. Those who do so close their eyes to the fact that the development of modern science has been over several centuries a fragmentation into an ever growing plurality of scientific approaches with no interest at all in a universal theory, but strong inclinations and inner forces to continue so in the foreseeable future. Philosophy of science would be better off, and more useful, if it acknowledges and studies the pluralistic constitution of science.

5.3 The Pluralist Constitution of Chemistry

What has been said about science in general correspondingly holds for a mega-discipline such as chemistry. Regarding the number of publications, chemistry has long been as big as the rest of the sciences altogether (Schummer 2004). The production of more than a million publications per year requires a breakdown into hundreds of specialized fields, if results are to be read and discussed in a scholarly manner. Many divisions resulted from disagreement on conceptual frameworks in the past. However, even if such breakdowns were once systematically achieved, later research frequently blurs or overcomes clear-cut boundaries, as the outdated distinction between organic and inorganic chemistry illustrates. Rather

than being reunited, typically those fields each follow their own paths because they have developed distinctive disciplinary approaches, research goals, and conceptual frameworks. Some focus on quantitative prediction as their major research goal, as in computer modeling. Others are interested in explanation by, for instance, studying the mechanism of chemical processes. Issues of classification, either of substances or of reactions, dominate many fields, whereas others look upon that from the specific point of improving synthetic capacities. There are fields of chemistry studying phenomena that probably do not occur outside the laboratory, as well as fields that define their identity by certain areas of nature, like bio-, geo- and astrochemistry, or of industrial application, such as pharmaceutical or polymer chemistry. Further, a broad range of chemical fields transgress disciplinary boundaries and adopt ideas, aims, and methods from their neighboring sciences, like physical chemistry and mathematical chemistry.

While such a kind of pluralism might discomfort the monist philosopher, it only illustrates the manifold goals and uses of science. The fact that the actual science pursues a variety of epistemic purposes, other than the so-called "truth of theories", in an undogmatic manner, makes it useful and flexible enough to address current and newly emerging problems. Even if we zoom in and look closer at the conceptual apparatus of individual fields, pluralism shows up.

Hasok Chang (2012) has shown in much detail for three important episodes in the history of chemistry – the Chemical Revolution, early electrochemistry, and the development of atomic and constitutional chemistry – how pluralist competition and interaction enabled the successful development of central concepts and theoretical approaches in chemistry. Rather than ending such competitions by electing a winner, chemists have frequently elaborated on the competitors and turned them into alternative models that are each tailored to specific aims and research questions. An almost arbitrary look into chemical textbooks reveals the obvious (Schummer 1998a). In inorganic chemistry, for instance, various theoretically guided concepts or models of what acids and bases are, compete with each other, such as those by Brønsted, Lewis, Pearson, and many others. Yet the competition is not about who is right or wrong, but about where exactly which model is more useful in explanations and predictions. Similar choices can be made between ligand theory and crystal field theory in chemistry of complex compounds; between the models of Freundlich, Langmuir, BET, etc. in adsorption theory; between collision and transition state theory in chemical kinetics; between a huge range of equations of state (from the simple ideal gas law, to the equations of van der Waals, Peng-Robinson-Stryjek-Vera, and dozens more) in thermodynamics; between molecular orbital, valence bond, and density functional theory in quantum chemistry, each including a variety of specific models; etc.

The case of molecular structure might illustrate further how the pluralism of models works in chemistry (Schummer 1998b). Since the mid-nineteenth century organic chemists have developed classical chemical structure theory that assigns to each compound a molecular structure, based on its elemental composition and chemical reaction properties. In this theory, a molecular structure is not simply a spatial arrangement of atoms, but an arrangement of so-called functional groups

that represent the substance's chemical reactivities, which in turn are modeled by a growing set of standardized reaction mechanisms. The theory does not only provide explanations and predictions of chemical properties, it also allows planning and guiding chemical synthesis of hitherto unknown compounds. Indeed, tens of millions of new compounds have been predicted and synthesized by that approach. In contrast, quantum chemical modeling of molecular structure provides a unique approach to the explanation and prediction of electromagnetic and many thermodynamic properties, but is still rather poor regarding chemical transformations. That is not only a theoretical division of labor according to different kinds of properties to be dealt with by different approaches. The case of chemical structure theory illustrates that chemistry is not only about explanations and predictions. Instead, theoretical concepts are also developed and judged here according to their potential for synthesis, a major activity of chemists for various, mostly nontechnological ends (Schummer 1997, 2004). Moreover, theoretical concepts are expected to provide a basis for classification, to distinguish unambiguously between myriads of substances (Schummer 2002). The various subdisciplines of chemistry have further developed dozens of different kinds of molecular models and representations, from solid state chemistry to biochemistry, that each serves specific disciplinary needs and purposes (Hoffmann and Laszlo 1991).

5.4 The Inevitability of Pluralism

There are two reasons why methodological pluralism is inevitable in chemistry: one relates to its multiple purposes, the other is grounded in the limits of chemical knowledge as a matter of principle.

The first reason is obvious from the aforementioned. Because chemistry pursues different goals, we need specialized approaches to achieve each one best. The argument requires different aims being logically independent from each other, such that achieving one does not automatically achieve the other. Although that is difficult to demonstrate in general, one can show at least for some instances that the simultaneous pursuit of different goals can easily run into conflicts. For example, a useful classification requires distinctive qualitative concepts, whereas precise predictions necessitate quantitative concepts. If synthesis is the main aim, all concepts must be operational such that theoretical conclusions can be translated into experimental operations, which is not required for classification, prediction, and explanation. Explanations in turn need causal concepts that are frequently obsolete in classification. Pursuing technological aims requires at least some utilitarian concepts that are useless and sometimes distorting in other projects, and so on.

If we accept the pluralism of aims or purposes in chemistry, we must reject the idea that there is a superior aim, say TRUTH, whose eventual achievement would automatically meet all the other epistemic needs best. Such a superior aim is not known in chemistry. If somebody claimed that, it could only be either the logical combination of all known aims, and thus would be obsolete, or the favorite purpose of

one specialized field, which for the whole of chemistry would then be equally ranked with all the other aims. However, although the different aims are logically independent from each other, the pursuit of one can be useful for that of others (Schummer 2014a, chap. 11). For instance, working on causal explanations can make predictions more reliable than those that are based on mere statistical correlations. In turn, improving predictive capacities, including merely statistical error estimates, considerably helps the design and control of experiments conducted for the purpose of explanation or synthesis. Also synthesis and classification can mutually benefit each other, when synthesis reveals new, unexpected substance classes or when classification allows one to derive synthetic goals. Similarly, technological aims frequently inspire explanatory, predictive, synthetic, or classificatory work, and vice versa. Although methodological pluralism is inevitable in chemistry, that does not mean that all approaches follow paths independent from one another. Instead, they can mutual benefit each other by complementary assistance, which is, like the modern division of labor in economics, much more beneficial for the entire endeavor of science than the pursuit of obscure aims such as TRUTH.

The second reason why methodological pluralism is inevitable in chemistry refers to its epistemic limits. Historically the limits of scientific knowledge were the central topic of epistemology, from medieval debates on the relationship between science and theology to Kant's *Critique of Pure Reason*, before it became outmoded by ambitious philosophies and popularizations of physics. However, an approach that does not know its limits and instead promises universal applicability without scientific arguments, belongs to speculative philosophy or simplistic popularization rather than to science. While it is the job of each science to define the limits of applicability of its individual theories or models (see below), it is up to epistemology to identify fundamental limits of knowledge that cannot be overcome.

There are several such limits of chemical knowledge (Schummer 2010), of which one is particularly important here: the unbridgeable gap between the concepts and objects of chemistry. The general issue has a long tradition in philosophy, most prominently in the metaphysical realism/nominalism debate (Sect. 5.7). However, in chemistry we have a privileged access of analysis that allows conclusions beyond metaphysical speculations. For, chemistry has addressed the realism/nominalism issue, which is sometimes misleadingly called the issue of natural kinds, by experimental means, largely unnoticed by mainstream philosophy. Rather than only adjusting our concepts to the world as it is, chemistry also adjusts the world to its concepts by creating experimental systems that best fit its frameworks (Schummer 2010). Most importantly, the objects of experimental investigations are the end results of sophisticated purification procedures: pure substances or fabricated mixtures thereof. Because every concept of modern chemistry, both empirical and theoretical, is based on the notion of pure substances, the strategy seems to be ideal. It has its price, however, because there are, strictly speaking, no pure substances in the material world, neither inside nor outside the laboratory.

In the natural world, a piece of matter is always a complex mixture whose compounds, in terms of pure substances, can be listed only with limited precision. For instance, one can identify a few thousand substances in a simple piece of soil,

knowing that this is only the tip of the iceberg. Moreover, while our theoretical understanding might grasp chemical reactions within mixtures of ten or twenty substances under certain conditions, it usually fails to provide comprehensive explanations and predictions beyond that limit. The drawback of adjusting matter in the laboratory to chemical concepts is that both our empirical and theoretical concepts are very limited to understanding the natural world. Even inside the laboratory, material samples never fully meet the conceptual ideal of purity, because of practical limitations of purification procedures and for thermodynamic reasons. Instead, any presumably pure substance can contain impurities at concentrations below the analytical limit. Matter, so to speak, resists purification at a certain degree and thereby chemical conceptualization. Because even the smallest impurity can have, through catalytic effects, a strong impact on chemical properties, there will always be uncertainty in any specific chemical statement.

Such uncertainties, both about natural and laboratory systems, can only be reduced by considerations of relevance, that under this specific condition and for that particular question this or that impurity in a given system is irrelevant. For instance, for many research purposes the gases of the air dissolved in pure liquids do not matter, for others they crucially impact the experiments. That most elements come as a mixtures of isotopes is negligible in many field of chemistry, in others it is essential. There are issues for which we may assume pure water to be simply H_2O, many others need to take into account its dissociation, and some even its complex dynamic structure that makes it look like a mixture of hundreds of species.

The complexity of matter forces us to take different perspectives depending on what we want to know. One might object that the limitations are only of practical nature and that future chemistry will push the limits towards the "ideal science", in which every piece of matter can be analyzed with ultimate precision and described by a "Theory of Everything" that takes any possible fact into account. However, apart from the insurmountable practical issues of generating endless information, that ideal runs into serious conceptual problems. From the point of view of ultimate precision, every piece of matter is unique and no longer a sample of a species. If we thus investigate one, two, or hundreds of samples, we could no longer draw general conclusions from our studies about a certain kind of matter, because the notions of both kinds and samples are no longer available. We would then lose the ability to build general concepts and provide general knowledge, on which science essentially rests. If, on the other hand, we later screen the endless information for what is relevant from a certain point of view and build corresponding equivalence classes in order to form general concepts and statements, we would just end up doing what science actually does: building a variety of different approaches depending on what is taken to be relevant. The "Theory of Everything", and its philosophical counterpart of radical nominalism, is therefore a useless and counter-intuitive idea in chemistry.

The two reasons for pluralism, multiple aims and epistemic limits, thus act in concert. Chemistry (and probably any science faced with complexity issues) can partially overcome its epistemic limits by diverging according to its different aims.

The following three sections look closer on what methodological pluralism in chemistry means for some exemplary philosophical issues: laws of nature,

reductionism, and realism. As much as mainstream debates, with their focus on mathematical physics, have presupposed methodological monism, so much will their concepts and views be useless, even obstructive, for the philosophical understanding of chemistry. As any approach that seeks understanding, also philosophy of science cannot evade the inevitability of pluralism and must develop distinctive approaches for the understanding of each discipline.

5.5 Models Versus Laws of Nature

The notion of laws of nature plays an eminent role both in the philosophy and popular representations of science, suggesting that their discovery is the primary task of scientists (for details on the following, see Schummer 2014b). However, at least for the past hundred years, it is hard to find a single law that has been formulated and called so in chemistry, and similarly in physics. Without strict terminological distinctions, chemists call their theoretical findings theories, equations, or, most frequently, models, for good reasons as will be seen below. Moreover, the many so-called laws from the nineteenth century do not meet the rigorous philosophical requirements such as universality and validity without exceptions that are usually associated with that notion. Even worse, all the so-called limiting laws of physical chemistry (such as the ideal gas law, Rault's law, Henry's law, and so on) are strictly valid only for the ideal case of zero concentration, i.e. for no single real case, which makes standard procedures impossible to fix the universality by limiting the validity through so-called ceteris paribus conditions. Philosophers of chemistry (Christie 1994; Christie and Christie 2000), considering all that a deficiency, have suggested a more liberal concept of laws of nature so as to cover chemistry by the conceptual apparatus of philosophy of science. However, the problem is not chemistry, but the philosophical misconception of science, according to which all disciplines would have to meet the standards set by philosophers of mathematical physics.

Historically the core of the experimental tradition of science, chemistry has developed its own pluralist methodology of models that radically differs from the monist mathematical tradition, out of which the notion of laws emerged (for the two tradition, see Kuhn 1976). Laws, on the one hand, are formulated with universal claims of truth, which can at best later be reduced by ceteris paribus conditions or extended by the reduction of other laws. Models, on the other, are developed on the approximate description of exemplary cases, which can be carefully extended only by modification and sophistication that include parameters to cover their particularities. While a law is the better the more universal it is, a model is improved by precisely calculating, testing, and limiting its area of intended applications with error estimates. There can be no two laws of nature competing with each other for long, because there is only one nature which any law tries to describe truthfully and completely. Different models for the same field of application can peacefully coexist and usefully complement each other, because they might employ different approximations or put different emphasis on different kinds of questions and aspects. Both laws and models are

comparable tools for explanations and predictions, but laws assume exclusive explanatory power while models can explain only those aspects they have been built to do so. Laws, if confronted with serious problems, have to be dropped altogether, which results in discontinuities of science and makes previous research appear useless, whereas models can be flexibly adjusted or supplemented by new models. While laws are inherently reductionist in the sense of methodological monism, models are developed in the vein of methodological pluralism.

The two methodological approaches, of laws and of models, are so diametrically opposed to each other that any attempt to mix them or to extend the concept of laws so as to include models runs into counterintuitive, if not absurd, results. Philosophers would do better if they keep the two opposing methodologies strictly apart, because the epistemological issues and their metaphysical implications of one methodology are largely irrelevant for the other.

5.6 The Monist Assumption of Reductionism

From the pluralist perspective, also the debate on whether chemistry is reducible to physics appears misleading. Terms like "chemistry" and "physics" nowadays refer to mega-disciplines, which each comprises not only a single theory but a plurality of conceptual and methodological knowledge traditions as well as the societal structures that bear the social identity of disciplines.

If we take, for brevity reasons, only the conceptual and methodological traditions that constitute the cognitive side of a mega-discipline, they are, in the case of chemistry, split into hundreds of different research fields (see above). Since they can today only be socially rather than cognitively united under the umbrella of a mega-discipline, it is more than questionable that an entirely different discipline could do better. On the level of sub-disciplines or research fields, there are differences regarding the conceptual apparatus, research aims, and methodological values. It is usually easier to find corresponding agreements between research fields of the same discipline than of different ones, with the exception of bordering areas such as physical chemistry and chemical physics.

How then about the reduction of a single theory of one discipline or subdiscipline through that of another? Nagel (1961, p. 351ff.) once raised the issue with two theories taken from physics, nonchemical thermodynamics and the kinetic theory of gases. In general, however, theories cannot be analyzed and judged in isolation from their aims, which considerably differ between the disciplines. If both serve different (sets of) aims and thus have different areas of intended applications, one cannot simply compare them or even judge one as superior (reducing) over the other (reduced). The idea of reduction of theories makes sense only if the area of intended applications of one is a subset of that of the other. In that case, however, it is hard to see how philosophers can contribute. In science, unlike in speculative philosophy, claims on the area of intended applications are to be made and judged by scientific arguments alone, which is the job of

scientists. In the pluralist world of modern science, there is no privileged model that is granted metaphysical status, i.e. the broad-brush entitlement of universality that exempt it from clearly delineating its field of application by scientific arguments.

Finally, if a theory of one (sub-)discipline is able to explain a phenomenon or property to the satisfaction of another (sub-)discipline, that counts as a successful case of interdisciplinarity, which makes all parts happy. A case in point would be the quantum chemical explanation of the specific electric conductivity or chemical bonding energy of a substance. Properties, particularly the operationalized ones in the experimental sciences, are not proprietary of a discipline but common ground. Interdisciplinarity consists in sharing and reconfiguring conceptual resources from different origins for the mutual benefit or the solution of a cross-disciplinary issue. Reframing such practice in terms of reduction of one discipline to another would not only miss the conceptual efforts required on both sides, but also introduce hierarchical thinking that is hostile to interdisciplinary collaboration.

In sum, it is difficult to make philosophical sense of the epistemological reduction of one discipline to another. The only cases that can reasonably be discussed, when the area of intended applications of one theory is a subset of that of another, are typical issues of scientific debate, for which philosophers have no particular competence to contribute. They do have, however, for investigating conceptual and methodological differences between disciplines, which makes interdisciplinarity issues a much more promising and useful field of philosophical studies than reduction.

5.7 Realism Revisited

Since the 1970s, philosophers of science have discussed a view they call "scientific realism". Although there exist now dozens of versions, they all share the opposition to "instrumentalism", the view that scientific concepts and theories are judged according to their usefulness regarding epistemic aims such as prediction, explanation, classification, synthesis, and so on. However, "instrumentalism" is a truism in science and elsewhere: the epistemic value of something is always assessed on the basis of whether it helps us pursue certain epistemic aims. Within the pluralist constitution of science, it is even necessary to point out for what particular epistemic aim a scientific concept or model is good for in order to improve the division of scientific labor.

The adherents of "scientific realism" instead seek intrinsic values in theories that are independent of epistemic aims, or any aim whatsoever. They claim that certain theories are in a not further explicable way "true".[1] The search for such theories

[1] If the truth conditions of a theory consist in all sentences that can possibly be deduced from the theory plus specific assumptions, as a standard view maintains, that would amount to all its possible explanations (postdictions) and predictions. Yet, "scientific realism" wants a theory to be more, making truth an obscure notion.

cannot be conducted for epistemic purposes, which would be "instrumentalism", but must be a purpose-free activity. The debate has, of course, focused on distinguishing the latest theories of mathematical and high energy physics (and strangely begun in the USA during the Cold War, when exactly that kind of research was heavily funded for military purposes). By excluding any purpose, including epistemic aims, they have created a very distorted image of science. In contrast, all scientists pursue aims, epistemic or not, and they use terms like "true" much more flexibly, depending on the discipline and always on how much the corresponding concepts have been successful in pursuing various epistemic aims. Moreover, by distinguishing the theories of physics among the vast plurality of research fields, "scientific realists" have not only repeated the received one-sided focus on theoretical science, but also tried to reformulate a version of physicalism. "Scientific realism" is thus only the latest desperate movement to uphold the flag of physicalist monism in the pluralist world of science.

It is therefore overdue to drop "scientific realism" and look for a concept of realism that is meaningful for the pluralist constitution of science in general and chemistry in particular. Hasok Chang (2012, ch. 4.2) has already argued in a similar vein that realism is not a matter of belief in the truth of a theory, but an active commitment to the pluralist pursuit of knowledge of the external reality. I will take a slightly different approach in the following sketch (for more details, see Schummer 1996) by returning to the original meanings of realism. In philosophy, realism has been a position opposed to either idealism, nominalism, or skepticism, depending on whether the reality of the outer world or the correspondence of our concepts and knowledge to the world is denied. If we find in the practice of chemistry institutionalized traits that conflict with those views, we have some clues of what realism means here.

Idealists believe in the reality of ideas or, more radically, that only ideas form reality. The view has thrived particularly within rationalism, which rejects sense perceptions and experience as reliable sources of knowledge, and instead seeks contact to its reality through intuition and logical constraints of reasoning. While that undoubtedly plays a role for chemists, most of them seek contact to reality first of all through experimentation in the double meaning of the word. One the one hand, they probe the behavior of material samples under the sophisticated control of the context in order to test or modify a conjecture. On the other, they playfully or systematically explore the behavior of material samples in search for unexpected, surprising results. In both cases, the behavior of the probed material world is considered independent from human will and planning, a material response rather than the intuition of an idea. That is a clear indication that experimental chemists reject idealism and instead favor the corresponding realism as their institutionalized metaphysical view. This kind of realism is fully compatible with methodological pluralism, because it does not matter what particular aim is pursued or what kind of conceptual framework is presupposed, as long as the general rules of experimentation are observed. In theoretical and computational chemistry, where results depend solely on the theoretical input or mathematical algorithms and some given data, that differs however. Thus, within the overall pluralism of chemistry, metaphysical

realism has been institutionalized in the methodology of experimental research, while theoretical branches follow a style that is more akin to idealism. The issue is no longer a matter of philosophical interpretation or taste, as it might have been still in the eighteenth century, but depends on what specific research field we look upon.

The second traditional opposition to realism, nominalism, claims that our classificatory concepts, while being useful ideas for certain human purposes, have no correspondence in the world. We might want to divide up the world into kinds and sub-kinds, but such divisions are only mental constructs rather than kinds whose differences are founded in nature. All that really exists are individual pieces of matter that can at best be related to each other by similarity relations. Originating in medieval metaphysics, it became a powerful modern position from the mechanical philosophy to Logical Positivism, which is difficult to refute in natural history. However, chemistry has long solved the issue for its own purposes by experimentally adjusting the material world in the laboratory to its concepts (Sect. 5.4). We divide up mixtures not by mental but by experimental analysis into compounds, and correspondingly compounds into its constitutional elements. And conversely, we make compounds not by mental compositions of properties, but by chemical synthesis. Although the results are not ultimately perfect for practical reasons, as mentioned before, the species thus created are reproducible in any laboratory at any time. No chemist denies that chemical elements and substances are real kinds rather than mental constructs. Even further, if chemists conceive of theoretical entities, i.e. chemical substances that do not exist yet, they reasonably believe in their potential reality, which is the most convincing case of "entity realism" (Schummer 1996, chap. 6), because they know how to realize them in the laboratory by theoretically guided synthesis, as has been done millions of times before. In sum, conceptual realism, as opposed to nominalism, is an unquestioned position in chemistry because it is deeply rooted in its experimental practice. As long as the general rules of experimentation are observed, species can be developed for different purposes and by different methods, such that conceptual realism is also compatible with pluralism.

The third view opposed to realism, skepticism, denies that we can achieve reliable knowledge about the world. From the aforementioned it immediately follows that this is an untenable position in chemistry. Because chemists, unlike mathematicians or philosophers, seek contact to the outer world through experimentation and because their concepts to describe the world are operationally based in experimental practice, which can be reproduced by anyone at any time, the knowledge thus achieved meets all conditions of objectivity and reliability one can reasonably wish for. Although that, of course, refers only to very basic experimental knowledge, it suffice to refute skepticism in general and to establish a foundation for epistemological realism. We can go further, however, if we drop the idea that theories must be either true or false, which is so vulnerable to skepticism. In the experimental sciences, theories or models, or more generally conceptual frameworks, are not the end but the means of science. Similar to the experimental apparatus, they are tools to probe the world, to pose precise questions for which we expect precise and reliable answers. Like any tools, their quality is a matter of degree, depending on their inner construction (conceptual clarity, logical consistency, degree of sophistication, easiness of use, etc.), and they can be more useful

for certain tasks and less so for others. Equipped with suitable conceptual and experimental tools, we can measure, for instance, binding energies, inter-atomic distances, activation enthalpies, and other theoretical values, which might lead to further theoretical explanations, classifications, predictions, synthetic strategies, etc. If the conditions and assumptions, which are part of any conceptual approach, are carefully listed, and premature generalization avoided, the skeptic has little to object to other than repeating the assumptions. But why should one expect unconditional knowledge from science? As a rule, scientific knowledge about the external world comes in the form: If we pose a certain question and take this method which includes these restrictions and those assumptions, we get that answer with that degree of certainty. Epistemological realism is thus not only compatible with, but even requires pluralism, because conceptual approaches need to be tailored to specific questions to provide precise and reliable answers. Philosophically speaking, the epistemology that is anchored in the research practice of chemistry is perspectivism.

Once we drop the obscure idea of "scientific realism" and look instead at what chemists do, philosophical realism turns out to be institutionalized in all its three traditional forms: metaphysical, conceptual, and epistemological.

5.8 Conclusion: The Advantages of Pluralism

In Sects. 5.2, 5.3, and 5.4, I have argued that pluralism is, as a matter of fact, the methodological constitution of science in general and of chemistry in particular and that it is inevitable for both practical and epistemological reasons. Against that background, pointing out its advantages over monism appears to be obsolete. However, the philosophy of science that has dominated for decades the debate has focused so much on a single, mono-purpose, and exceptionally uniform subdiscipline, mathematical physics, that it has created a strong taste for monism which is difficult to convince of what is obvious. The unspoken implication of monism is that the actual science, with its ever growing divergence into methodologically different disciplines, subdisciplines, and research fields, is a deeply irrational enterprise. In contrast, I suggests that science is a very rational endeavor. That is not an opportunistic statement seeking agreement from scientists. For, if pluralism is both inevitable and serves various epistemological needs that scientists actual have, only a fool would do without it.

There are many other benefits of pluralism, some of which have already been discussed in detail by Hasok Chang (2012, chap. 5.2) or mentioned before. First of all, if we acknowledge that biology, physics, chemistry, geology and so on (as well as correspondingly their various research fields) have different subject matter and different research aims that require different methods, it is obvious that monism can pick only a single aspect and disregard the rest. Pluralism instead allows a non-hierarchical division of labor, which in most fields of society is the most effective and successful approach. Moreover, as new kinds of issues arise, either out of the research process or by societal demand, science can flexibly adjust by

extending old or developing entirely new approaches. The monist philosopher must ignore all that or reject it as "applied" research not worth studying. Sticking to the glorious past of less than a handful of physical theories, monist philosophy has developed an extreme conservatism without contact with contemporary science and its enormous creativity. In contrast, pluralist philosophy can not only appreciate this aspect but also study its manifold dynamics.

When the division of labor is not so clear-cut, such that different approaches are required to collaborate in a multi-aim project, they can share and combine their resources. Pluralism provides the analytical resources to understand possible barriers of interdisciplinarity, in terms of their different conceptual and methodological views, and mediate between them, whereas the only monist answer to such problems is the hierarchical order by way of impossible discipline reduction. Moreover, combining resources and perspectives has the further advantage that it can create new conceptual and methodological approaches. Because scientific research is all about creating novel understanding, pluralism thus provides the best framework for the methodology of discovery and innovation. In contrast, monist methodologies have largely focused on the futile search for a universal logical method for the retrospective justification of what is already known, e.g., the support of a theory. That, however, considerably differs among disciplines as diverse as, say, geology and mathematics, and among specific research fields, depending on their respective research aims and methods as well as the intended usage of their theories.

Surely competition plays an important role in pluralist science too. Two approaches or models may compete with each other on which is the best one to achieve a certain aim. Such debates help sharpen and elaborate the approaches, or inspire entirely new ones. It may turn out that their aims and areas of intended applications differ more than was expected at first, such that they can supplement each other. If the difference is more fundamental, competition continues, which might result in different research schools and traditions that each develop valuable conceptual and methodological resources further. Because the future of science is for reasons of principle not predictable, including future aims and research questions, final decisions on such competitions would be an unreasonable strategy in science. However, monist philosophy requires such a decision, because there is supposed to be only one "truth". It imposes the inappropriate winner/loser metaphor on science to purge it from the valuable conceptual and methodological resources of the alleged losers. In contrast, pluralist philosophy cannot only study the various ways of solving competitions, but also appreciate continuing competition for epistemological reasons. The more approaches we have, the richer is our perspectival understanding of the world; and the more precisely the approaches are limited, the more reliable is our knowledge. Thus, pluralism allows for two-dimensional progress in science, whereas monism makes the unreasonable demand that scientists produce both methodological and content-based knowledge that would most likely have to be dropped in the future.

Finally, pluralism provides valuable lessons for philosophy of science drawn from the pluralist constitution of science in general and of chemistry in particular. If a philosopher makes general statements about science, the pluralist asks: for which

discipline or research field is your statement valid? That prevents reckless generalizations, broadens one-sided views, and allows one to estimate the relevance of philosophical topics among the diversity of science. Three cases in point have been discussed in this paper: the unreasonable extension of the notion of laws of nature from mathematical physics to science in total; the monist assumption in the debate about reductionism; and the misleading conception of "scientific realism". Focusing on the actual scientific practice, which is inextricably linked with human aims and purposes, philosophical pluralism is rather in the tradition of pragmatism and strictly opposed to logicism and idealism in the Kantian and Hegelian style. It brings topics to the fore that both matter in science and to which philosophy can make useful contributions, such as the methodology of models, the issues of interdisciplinarity, and the institutionalized forms of realism in scientific practice. Without repeating the mistake of blind generalizations, the philosophical perspective on chemistry can thus help enrich philosophy and explore its resources for the benefit of science.

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Chapter 6
Pragmatism and the Philosophy of Chemistry

Joseph E. Earley Sr.

6.1 Introduction

"How is it possible in a universe consisting entirely of physical particles in fields of force that there can be such things as consciousness, intentionality, free will, language, society, ethics, aesthetics, and political obligations?" John R. Searle suggests that this is the single overriding question in contemporary philosophy—but also notes that "many, perhaps most, contemporary philosophers do not address it directly" (Searle 2010, 3). Joseph Margolis (2012, 129 ff.) agrees with Searle's assessment of the importance of that question—but he rejects the response to it that Searle proposes. Instead, Margolis claims that the philosophical approach called "Pragmatism" is well on its way to resolving the problem that Searle identifies.

Charles S. Peirce (1839–1914) (the family name is pronounced '*purse*') is generally regarded as the founder of philosophical Pragmatism. Arguably, this characteristically American approach is the only non-religious philosophical school that originated outside Europe—but it may now be cultivated elsewhere more than it is in the United States. Peirce did his graduate studies in chemistry, and he identified himself as a chemist throughout his career. Peirce worked for many years in The United States Coast Survey, mainly carrying out precise geophysical measurements: his voluminous philosophical publications deal more with logic and semiotic[1] (the theory of signs) than with chemistry. It is now clear that the

[1] Peirce considered 'semiotic' to be a discipline parallel to 'logic.' He continued to develop and modify his theory of signs throughout his life, several times rejecting his earlier efforts because of difficulties he had identified. However, Jacques Derrida and others have continued to apply Peirce's early theories of signs under the designation 'semiotics' (Short 2007, 45). Peirce's theory of signs (semiotic) is discussed later in this paper.

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nineteenth-century investigations by which chemists solved the problems of stereochemistry were pragmatic[2] rather than theoretical (Ramberg 2001). Clevis Headley (2013) convincingly argued that features that distinguish philosophical Pragmatism from other approaches derive directly from Peirce's deep experience in chemical-laboratory practice.

Peirce is now recognized as one of the most original and significant thinkers that America has produced (Moore and Robin 1994, ix). Philosopher and educational leader John Dewey (1860–1952) was a prominent exponent of philosophical Pragmatism during the 1920s and 1930s, but that mode of thought became less fashionable during the ascendancy of analytical philosophy in the 1950s and 1960s. Richard Rorty (1931–2007) and Hilary Putnam (b. 1926) sparked a revival of interest in Pragmatism in the last quarter of the twentieth century. This chapter aims to show that Pragmatism is relevant to current problems in philosophy of chemistry. After introducing some main themes of Pragmatism and aspects of current philosophy of chemistry we will return to Searle's question.

6.2 Philosophy as Un-modern

Peirce did not produce a comprehensive summary of his thought, but in the early 1940s John Dewey drafted a book that reviewed some main points of Pragmatism. Unfortunately, Dewey misplaced his nearly-completed manuscript. That work was recently found, edited, and published (Dewey 2012). In it, Dewey vigorously criticized other types of mid-twentieth-century philosophy claiming that obsolete concepts, distinctions, and problems remain imbedded in contemporary thought—even though results and practices both of science and of philosophy clearly require otherwise. Following Peirce, Dewey stressed the important fact that, necessarily, human activities are *socially* located—therefore all philosophical doctrines are influenced by the cultures in which they originate. Dewey called much of mid-twentieth-century philosophy "*un-modern*" since it had failed to recognize that basic concepts of the Western philosophical tradition had been formulated under assumptions that we now know to have been wrong. When established cultural patterns are challenged by technological change or external influence, new philosophical approaches may emerge—as they did in Classical Greece, Medieval France, and Renaissance Europe. However, even such major conceptual innovations are generally framed, considered, and discussed in terms of categories originally developed for other purposes. Such conservatism often leads to misunderstanding—and to distortions which are difficult to identify and to remedy.

The dichotomies that abound in philosophy—subject/object, individual/property, contemplation/action, mind/body, essential/accidental, fixed/changeable, theory/practice—generally identify mere sections of some continuous variation—parts

[2] This word (un-capitalized) refers to a practical attitude rather than to Peirce's philosophical approach (capitalized here).

selected under the influence of a local culture. Societies in which a small and leisured elite dominated the majority—such as slave-based ancient societies and patronage-driven early-modern ones—accorded higher dignity to theory over practice. Dualities of this sort tend to persist long after the disappearance of factors that had brought about their adoption. Failure to revise simplifying assumptions is a related problem. Results obtained *synchronously*—at a single instant, as in a photograph—are generally quite different from results that would have been obtained by *diachronic* investigation—considering time-variation.

The quest for *true and certain* knowledge ('the epistemology problem') has been a usual feature of ancient, medieval, and modern conceptual systems (Dewey 2012, 130 ff). Both René Descartes and John Locke sought to ground their systems on bedrock. Immanuel Kant's *transcendental a priori* aimed to provide a firm basis for timeless truth. George Hegel substituted diachronic notions for synchronic ones, but retained 'the absolute.' Following Peirce, pragmatists deny that any conceivable description of the world could possibly be complete and accurate enough to be adequate for *any and all* purposes. There is no '*God's-Eye View*.' On that basis, pragmatists reject Kant's notion of 'the-thing-in-itself' and the related notions of ontological and epistemological descriptions (how things are versus how things appear to be). Certainly, accounts could consider underlying mechanisms or not, and could be more or less adequate with respect to a specific goal of inquiry—but there is no *fully-adequate* ('ontological') description.

6.3 Inquiry as Evolutionary Adaptation

Human knowledge is connected with effective action. Some understandings foster successful action, others lead to failure. *The Pragmatic Maxim* connects many aspects of Pragmatism.

> Consider what effects, that might conceivably have practical bearings, we conceive the object of our conception to have. Then our conception of these effects is the whole of our conception of the object (CP 5.402).[3]

Pragmatists point out that we learn about the world we inhabit—and also about our own capabilities and limitations—by interacting with and exploiting our surroundings, including members of our own species. Other animals sometimes modify 'found' objects to increase their usefulness: humans have developed such abilities to high levels (e.g., pharmaceutical chemistry, nano-electronics, behavioral conditioning). We flourish through cooperation—and also through competition. *Language* fosters cooperative action by persuasion, blandishment, or threat—and thereby facilitates success in inter-group competition. Successful actions and strategies become habitual. Each human grouping has a complex *culture* made up of shared habits—including language, tool-use, and communal ritual.

[3] This reference is to paragraph 402 in volume 5 of *The Collected Papers of Charles Sanders Pierce*. Cambridge, MA: Harvard University Press (1931–1935, 1958), also published electronically.

All biological organisms have adaptations that enable them to search for, and perhaps to acquire, what they need to live, reproduce, and prosper. Primates communicated using vocal signals for long eons before the emergence of *Homo sapiens* about 200,000 years ago (McBrearty and Brooks 2000). The anatomies of the larynxes of fossil hominids (Lieberman et al. 2002) demonstrate that as early as 700,000 years ago strong selection-pressure favored those individuals or groups that were adept at the use of proto-language (McBrearty 2007, 142). Significant *mutual* influence of genetic and cultural factors has been characteristic of the evolution of the ancestors of *Homo sapiens* (Richerson et al. 2010). Explicit knowledge depends on speech—and language is essentially social. Voiceless language-use enables *imagination* of situations that never occurred. When we imagine better ways to act, or when formerly-successful habits no longer work, we sometimes resort to *inquiry*—detailed investigation of specific issues. In favorable cases, inquiry may realize imagined improvements or resolve perceived difficulties, but every such achievement destabilizes other aspects of culture. Human behavior-patterns must continually adjust to cultural change. (The Red Queen[4] rules.)

Transmission of habits between generations and within and among communities depends on narrative, and is never error-free. Results of any inquiry can be extended and modified by findings of subsequent related inquiries. Outcomes of inquiry are never complete or certain. We do not know the entire and indubitable truth about any topic: all human knowledge is, at best, correct as far as it goes, or adequate for this or that purpose (da Costa and French 2003).

Peirce considered that: "The real is that which is not whatever we happen to think it, but is unaffected by whatever we may think of it" (CP 5.430). He held that the results of inquiry tend to converge on progressively better approximations of the real, but final convergence would require indefinitely wide and long inquiry. We may expect that well-established science has arrived at fairly-adequate notions of reality—but this cannot be guaranteed.

We deal with problems by actions—described by verbs (we *attack*). Adverbs specify aspects of actions (they react *rapidly*): adjectives describe qualities of objects (their runners are *fast*). Eventually, we *reify*—postulate objects from aspects of action (their *swiftness* did us in). Dewey (2012, 203 ff.) advised philosophers to be wary of pitfalls connected with progression from verb to adverb to adjective to noun. Descartes illustrated the error Dewey warns against when he postulated a *res cogitans*—a substantial *mind*—to account for successful human action. The fact that we can "Mind the Gap" does not mean that such an entity as 'mind' actually exists.

Inquiry gave rise to philosophy and eventually resulted in science. On this basis, language, intentionality, and human inquiry are all analogous to the elaborate behavioral adaptations that other organisms use to survive, reproduce, and flourish. Philosophy and science should be regarded as closely-related and highly-evolved human cultural adaptations.

[4] 'A slow sort of country!' said the Queen. 'Now, HERE, you see, it takes all the running YOU can do, to keep in the same place. If you want to get somewhere else, you must run at least twice as fast as that!' (Carroll 1872, Chapter 2).

6.4 Peirce's Logic of Relations

Athletes in team-sports often refer to '*good chemistry*'—a cooperative spirit that contributes to winning tight games. Chemical properties involve *relations* among substances. Both as a science and as a practical art, chemistry characteristically deals with relationships—arguably, focus on relationships is a *defining* feature of chemistry. As a student of chemistry, and also as the son of one of America's leading mathematicians (Harvard Professor Benjamin Peirce), Charles Peirce had a lively interest in the *logic of relations*: his pioneering work in this field made the development of modern symbolic logic possible.

Each relation involves a number (n) of relata—it has an '*adicity*.' Monadic (n = 1) relations are 'properties' (or 'qualities' or 'attributes'). Ordinary relations are diadic (n = 2) or triadic (n = 3). Relations with four or more relata are properly considered as combinations of relations of lower adicity.[5] Peirce in 1885 and Gottlieb Frege in 1879 independently introduced two innovations (quantification and use of variables) that distinguish modern logic from its Aristotelian ancestor: $\exists\, x = for\ some\ x; \forall\, y = for\ all\ y$ (and $Rxy = x\ bears\ relation\ R\ to\ y$). Peirce's innovations were recognized by leading logicians before 1890, but Frege's work was overlooked until Bertrand Russell called attention to it in 1910.

Some relations are symmetric so that $Rxy = Ryx$. But, if John loves Mary, Mary may or may not love John. Relation Rxy sometimes is reducible (so that $Rxy = Px + Qy$) but diadic relationships are not generally reducible to (decomposable into) combinations of monadic properties ($Rxy \neq Px + Qy$). The same is true for triadic relationships. Peirce cited an analogy between chemical valence and the logic of relatives: "A chemical atom is quite like a relative in having a definite number of loose ends or 'unsaturated bonds,' corresponding to the blanks of the relative" (CP: 3.469). He developed a Method of graphically representing logical relationships including the logic of relatives. This 'Method of Existential Graphs' was not well-received by contemporary logicians but later had important applications in digital computation.[6]

[5] Peirce wrote as if he had a rigorous proof of this, but never published such a proof. Presently-known proofs are not straight-forward.

[6] Peirce developed an approach to experience that explicitly avoided mechanistic explanation: he called this 'Phaneroscopy.' This method was analogous to Phenomenology, developed independently by Edmund Husserl at roughly the same time. Peirce distinguished three modes of being—the three Phaneroscopic Categories. "Firstness is the mode of being of that which is such as it is, positively and without reference to anything else. Secondness is the mode of being of that which is such as it is, with respect to a second [item] but regardless of any third [item]. Thirdness is the mode of being of that which is such as it is in bringing a second [item] and a third [item] in relation to one another" (CP 8.328). A certain color, say fire-engine-red, would be a First. Firsts are potentials—many things might or might not be red. Any bipolar interaction, say some percipient detecting red, illustrates secondness. Struggle and resistance are usual features of Seconds. Seconds correspond to actuality—entities are Seconds. A percipient interpreting red as a stop-signal would constitute a Third. Thirdness corresponds to generality—laws, purposes, and intentions are Thirds (Short 2007, 60–90).

6.5 Determinants of Irreversible (*Finious*) Change

Aristotle counted any adequate response to a why-question as a cause (*aitiā*) (*Physics* 194b, 18–20)—but he also made a clear distinction between *efficient* causes (change-initiating agents) and *formal* causes (arrangements necessary for events to occur). Robert Pasnau (2004) carefully described how, during the rapid development and subsequent slow decline of medieval Scholastic Philosophy, the understanding of the Aristotelian concept of *substantial form* gradually changed away from its original (purely formal) Aristotelian meaning and increasingly acquired overtones of efficient agency. He concluded that further modifications in the usual philosophical understanding of cause that subsequently occurred should be interpreted as continuations of that earlier trend. With the success of Newtonian physics interactions similar to events on billiard tables (where precisely-determined impacts yield exactly-predictable results) came to be considered prime exemplars of causal processes. *Efficient* causality took over the designation of cause. Most philosophers relegated any other factors that might be involved in answers to why questions to subordinate status or to oblivion. Alicia Juarrero (1999) persuasively argued that the restricted notion of causality that was adopted with the rise of modern science is an impoverished one—quite inadequate for analysis of complex questions of properly philosophic interest, such as those that concern human action. Billiard-ball causality, she observes, is not much use in "telling the difference between a wink and a blink."

Mario Bunge, like other philosophers, does "restrict the meaning of the term cause to *efficient cause*, or extrinsic motive agent, or external influence producing change" (Bunge 1959, 33) however he also recognizes that causation "is only one among several types of determination; there are other types of lawful production, other levels of interconnection" (30). He distinguishes between *causes* (effective agents—the *how* of things) and *reasons* (rational explanations—the *why* of things) pointing out that these two notions are often confounded. Bunge notes: "The identity of explanation with the disclosing of causes is even rooted in the Greek language, in which *aition* and *logos* are almost interchangeable since both mean cause and reason. The confusion of cause with reason, and that of effect with consequent, are, moreover, common in our everyday speech" (Bunge 1959, 226–227), but more recently, Bunge observed: "From the point of view of cognitive neuroscience, reasons for acting are efficient causes" (Bunge 2010, 224).

In many (perhaps most) biological examples, causes and reasons cannot be distinguished easily, if at all. "When a trait evolves through intersexual selection, the source of selection is itself an evolving character. The peacock's tail evolves through the mating-preferences in peahens and those preferences coevolve with the male trait" (Laland et al. 2011, 1512). Whenever *reciprocal determination* makes it impossible cleanly to distinguish causes from reasons, restricting causality to *efficient* causes (as philosophers recommend) is not appropriate.

6.6 Determination in Finious Processes

Thomas L. Short (2007, 105–107) observed that the narrowness of the contemporary philosophic understanding of causation (a baleful influence, he says, of David Hume's ghost) has had unfortunate effects—but he also called attention to an alternative understanding of causality that Peirce developed.[7]

The kinds of interaction that classical mechanics deals with have time-reversal symmetry (viewers have no way of deciding whether a video of billiard-ball collisions is running forward or backward). But natural processes often *proceed in one direction only*. Spark-induced explosion of a mixture of H_2 and O_2 loudly and rapidly produces H_2O vapor: the reverse reaction is unobservable. Peirce calls such unidirectional processes *finious*; Short suggests the designation *anisotropic*; chemists call such changes *irreversible*. Pierce held that in irreversible processes an alternate kind of causal process is of central importance—"that mode of bringing facts about according to which a general description of result is made to come about, quite irrespective of any compulsion for it to come about in this or that particular way; although the means may be adapted to the end" (CP 1.211). This corresponds to understanding a cause as reason rather than as agent. Peirce considered that Darwin's account of the origin of biological species exemplifies this alternative mode of result-determination.

Natural selection gradually (and irreversibly) eliminates whichever characteristics of organisms are not suited to the conditions that prevail. Such reduction (culling) of possibilities eventually produces one particular determinate result—which one of the many possible outcomes is actually produced depends on contingencies of culling rather than only (or mainly) on actions of underlying agents.

> . . . there remains little doubt that the Darwinian theory indicates a real cause, which tends to adapt animal and vegetable forms to their environment. A very remarkable feature of it is that it shows how merely fortuitous variations of individuals together with merely fortuitous mishaps to them would, under the action of heredity, result, not in mere irregularity, nor even in a statistical constancy, but in continual and indefinite progress toward a better adaptation of means to ends (CP 7.395).

> Natural selection works in such a way as to produce adaptation of life-forms to their circumstances: this general aim does not determine in what particular way it is to be brought about, but only that the result shall have a certain general character. The general result may be brought about at one time in one way, and at another time in another way (CP 1.211).

Peirce considers that each effective selection-criterion is a *general* rather than a *particular* (a universal rather than a substance). Each such criterion might be

[7] See also Reynolds 2002.

called a *controlling general*—an outcome-determining universal. By this means 'structures'—closures of relationships that have the property of engendering future versions of the same closures—would have result-shaping effects, although they would not be agents. Peirce's interpretation of Darwin's theory featured grounding causality by universals. According to this view, natural selection operates to amplify those features of a system that correspond to stability, under the conditions that prevail. Since organisms that pass the selection test may have many differences that are irrelevant to that test, the condition of persistence that this criterion involves is not a specific individual requirement but a rather more or less vague general condition—a universal.

In this way, a universal may have efficacy that is 'causal' in a broad sense. In other words, if a certain state-of-affairs results from *selection* on the basis of some criterion then that criterion (a universal) is a determinant (a cause in a general sense) of the state of affairs. To the extent that closure of a network of relationships of components is a prerequisite for the stability of entities, that closure is also a *necessary determinant* of that states of affairs[8] that it engenders. In order for recognizing anisotropic or finious determination, some temporal process must restrict the range of possible future states open to a system, blocking some but not others. If such an *equivalent to selection* accounts for the existence of a structure, then that structure may properly be termed a determinant—a cause in a sense that is more general than philosophers recognize.[9]

Several detailed mechanisms may achieve similar or equivalent results. For each conceivable way of achieving a stable dynamic coherence which works well (under the conditions which prevail) many imaginable variant arrangements would also succeed—but a much larger number of possible variations would not work successfully. Systems complex enough to contain one accessible route to closure typically contain many such ways to achieve dynamic stability (Kauffman 1993, 1995). In addition, if a viable dynamic coherence does exist, it turns out that the same coherence may be reached by several diverse historical routes. Commonly observed biological convergence ('homoplasy')—genetically unrelated species have arrived at similar biological structures through vastly different evolutionary pathways[10]—suggests that long-term viability is rare among possibilities.

[8] Bishop's (2012) account of the philosophic significance of nonlinear dynamics is consistent with this interpretation.

[9] This summary avoids the designation '*final causality*' that Peirce used for this mode of influence—in order to forestall confusion of reason with purpose, and to discourage the erroneous notion that reasons must be purposes of conscious agents.

[10] For instance, the fossil record demonstrates apparently-identical saber-toothed species of both mammals and marsupials (Conway Morris 2003).

6.7 Peirce's Theory of Signs

Peirce published a theory of signs ('semiotic') as early as in 1868–1869 (W2, 193–272).[11] Peirce subsequently recognized serious problems with his early semiotic and made significant revisions in 1885 and again in 1903.[12] At his death in 1914, Peirce left a number of partially-completed manuscripts including further major revisions of the theory of signs. T. L. Short (2007) produced a version of Peirce's theory of signs based on unpublished drafts, especially those written in 1907.

According to Short's reconstruction of Peirce's mature system, a motorist stopping after noticing a red traffic signal would be described as *R interprets X as a sign of O*—where R (the Interpretant) is the action of stopping, X (the Sign) is a particular red, and O (the Object) is a prudential, customary, or legal obligation. Short's version of Peirce's mature semiotic recognizes that semeiosis occurs *in a context*, that context being one of *purposefulness* (Short 2007, 158). According to Short's version of the later Peirce, whenever some feeling, thought, or action (R) interprets a particular X as a *sign* of O (an object, broadly understood) that interpretation must be made in the context of a *purpose*, P. A purpose (or habit) of acting in prudent, customary, or legal ways must exist for stopping at a red light to make sense.

In 1909, Peirce wrote:

> A Sign is a Cognizable that, on the one hand, is determined (i.e., specialized, *bestimmt*) by something *other than itself*, called an Object . . ., while, on the other hand, it determines some actual or potential Mind, the determination whereof I term the Interpretant created by the Sign, that the Interpreting Mind is therein determined mediately by the Object (EP 2:492).[13]

Notice that, in this passage, the Object *determines* the Sign, which, in turn *determines* the Interpretant. These determinations cannot be made by efficient causality. Functioning of signs depends on a purposeful context: the several determinations referred to in this passage must function through the finious causal mode outlined above.

Short does not spell out the means by which the purposes effect the selection on which finious determination depends, but examples can be seen in several types of scientific investigation. In biological systems upper-level coherences (say, the 'lekking' mating-rituals of tropical bower-birds) establish constraints that

[11] 'W2' is Volume 2 of *The Writings of Charles Sanders Peirce, A Chronological Edition*. Peirce Edition Project, eds. Bloomington, Indiana University Press, 1982–2000. In the publication reproduced in W2, 193–272, Peirce vigorously attacked all types of modern philosophy that descend from the work of Descartes, and claimed that we have no valid way of deciding what qualifies as 'an intuition.'

[12] However, as mentioned earlier, Jacques Derrida and others have continued to apply Peirce's early theories of signs under the designation '*semiotics'* (Short 2007, 45).

[13] EP refers to *The Essential Peirce: Selected Philosophical Writings*. Peirce Edition Project, eds. Bloomington: Indiana University Press, 1992 and 1998.

discriminate among lower-level characteristics, fostering some and eliminating others. (Dull-colored or non-displaying male bower-birds have no descendants.) Well-trained drivers ignore lights of many shapes and colors, but actively respond to (interpret) bright red circles. The training and experience of the driver *determine* her response, but as a reason rather than as an agent.

6.8 Nominalism Rejected

One of the main themes of Peirce's work was an attack on '*nominalism'*—the erroneous doctrine of fourteenth-century Ockhamists (and present-day analytical philosophers) that only individuals 'really exist'—this is to be contrasted with the *'realist'* opinion that some composite entities are 'real.' Dewey describes a usual, but highly damaging, result of nominalism:

> Ability to regulate, to guide and direct, the ongoing course of life-experience, as well as furtherance or prevention of occurrence of this or that special event, depends on breaking down the actual total event into a number of lesser events. But the history of human beliefs shows that two connected errors have accompanied the performance of this necessary task. . . . [T]he events which are analyzed into more minute events have been assigned a secondary degree of reality, and the actions in virtue of which the lesser ones constitute the original gross event are lost from view, or what is even more harmful, are treated as themselves simple or elementary static entities. It is one of the functions of philosophy to recall us from the results of analyses, which are made for special purposes, to the larger, if coarser and in many respects cruder, events which alone have primary existence.[14] (Dewey 2012, 324)

Peirce maintained that "the nominalist error" has wide significance.

> . . . though the question of realism and nominalism has its roots in the technicalities of logic, its branches reach about our life. The question whether the genus *Homo* has any existence except as individuals, is the question whether there is anything of any more dignity, worth, and importance than individual happiness, individual aspirations, and individual life. Whether men really have anything in common, so that the community is to be considered as an end in itself, and if so, what the relative value of the two factors is, is the most fundamental practical question in regard to every institution the constitution of which we have it in our power to influence (CP 5.38).

Searle's question with which this paper began contains a subordinate clause—"in a universe consisting entirely of physical particles in fields of force." The word 'entirely' in this clause, if taken seriously, would wipe chemistry completely off the map of significance. Chemists have good reason to be wary of nominalism. For Searle, nominalism needs no supporting argument: facts inconsistent with that approach are invisible to him. However, if the world consists *entirely* of particles in fields then John R. Searle does not exist.

[14] At this point Dewey added the footnote: "It is one of the merits of C. S. Peirce that he appreciated so thoroughly this aspect of philosophy. . . ."

6.9 Philosophy of Chemistry

Even though Charles S. Peirce was both a chemist and a significant philosopher, only a few papers in philosophy of chemistry refer to his work. Charles Siebert (2001) pointed out that Peirce's juvenile adventures in a home chemistry laboratory profoundly influenced his future development. Jaap van Brakel (1994) considered Peirce's 'Tychism'—the doctrine that "absolute chance is a factor in the universe" (CP 6.201)—and concluded that Peirce's belief in chance was "limited" since he held that: "Everyone knows that chance has laws and statistical results follow therefrom" (CP 6.606). On this basis, Peirce's Tychism anticipated recent interest in the practical importance of highly-improbable events (Taleb 2010).[15] Also, van Brakel (1998) discussed Peirce's concept of *natural kinds,* and decided that "Pierce's views are consistent with a form of pluralism in which the difference between natural and non-natural classes disappears" (38–39) and that the "ultimate end of inquiry" must be "pluralistic" (41). He also included incidental references to Peirce in his book on philosophy of chemistry (van Brakel 2000).

Chemists switch easily and smoothly among several types of discourse. They are comfortable dealing with materials in microgram quantities and also, on occasion, with barge-loads: they deal conceptually with truly immense macro-molecules and also with submicroscopic diatomic molecules and their much smaller constituents—electrons and nuclei. Chemists determine which entities they will consider depending on the question they are investigating. There is no 'universe of discourse' set up in advance of chemical investigation. Chemists are quite content to postulate existence of some new entity (a complex, an intermediate, an eximer, an excited state, a hybrid orbital, ...) if doing so makes sense of data already in hand, *and also* suggests additional investigations which might confirm or put into question the existence of the postulated entity. There is no preset fundamental level of chemical discourse: the level of discourse is chosen to facilitate achievement of the purpose of the investigation. Such purposes include (but are by no means limited to): devising a new synthesis for a natural product, discovering a drug to foster (or impede) a biological process, determining the accuracy of a theoretical prediction, exploring the range of conditions under which a new process occurs. Chemists shift among levels so effortlessly and (generally) unconsciously that philosophers and other non-chemists may fail to appreciate the consequences of this cultural feature.

Lee McIntyre (2007) expressed the widespread opinion that chemical discourse mainly concerns 'epistemological' description of how things appear, and rarely if ever attains to the 'ontological' description that is (presumably) characteristic of more-fundamental sciences. This opinion seems to be characteristic of the

[15] Van Brakel also refers incidentally to Peirce in his volume on philosophy of chemistry (van Brakel 2000).

nominalism that Pierce repeatedly attacked. Some chemists (especially those exposed to philosophy) may formally endorse nominalistic views, but chemists generally guide their professional activities by understandings similar to those of Bishop and Atmanspacher (2006, 1755), who describe *contextual property emergence*—by which upper-level properties derive from the *context of constraints* on a system as well as from properties of less-extensive entities that constitute underlying levels. Upper-level constraints typically remove degeneracies that characterize lower-level situations and thus lead to *stable* states. Such constraints are designated *contextual determinants*.

Olimpia Lombardi and Martin Labarca (2005)[16] maintained that entities at several chemical levels should be taken with full seriousness. In so doing, they retained the ontological/epistemological distinction, used Kantian vocabulary, and, in passing, indicated that "Noumenal Reality" exerts influence (their Figure 1, p. 145). Although these authors expressly rejected the notion of 'The God's-Eye View' they did not draw the inference that all that exists for us to know is *how things behave* under this or that set of circumstances. Dewey might consider use of inherited vocabulary by these authors to exemplify philosophical "un-modernism." However, in this case, this conservatism does not appear to have influenced the authors' argument.

Meanings of important terms often change greatly across the centuries, but chemists and philosophers of chemistry tend to anachronistically use more-recent meanings for important words in interpretation of earlier authors who had quite different understanding of the connotation of the same terms. For instance, the Greek words *hyle*, *aitia*, and *ousia* are now generally translated into English as 'matter,' 'cause,' and 'substance,' respectively—but the contemporary meanings of each of those terms to English-speakers is quite different from the significance the original words had for ancient Greeks (and often also for authors in other historical periods). In particular, the designation "matter-theory" that historians of chymistry routinely use (e.g. Garber 2007) to describe a fundamental outlook on nature seems unfortunate, since this usage employs a quite-modern notion of 'matter' (as a type of independent existent) that would not have been recognized by Medieval and Early-Renaissance workers—for whom 'matter' (*hyle*) would have been a more or less abstract 'principle' (*archē*) rather than an independently-existent substance (*ousia*).

As Dewey (2012, 159 ff.) points out, continued use of obsolete categories may raise philosophic problems difficult to recognize and to repair—but a different but parallel error may be even more harmful. Novel findings that do not fit preexisting categorial schemes may be effectively invisible—remain ignored for some time. Philosophy of chemistry has no immunity from this difficulty.

[16] See also Liwowicz and Lombardi (2013).

6.10 Process Structural Realism[17]

Some philosophic systems (e.g., Aristotle's) consider objects that retain their identity through time ('*substances*')[18] as fundamental, others (e.g., Whitehead's) deny that such coherences are so basic but still consider them important: "The Universe achieves its values by reason of its coordination into societies of societies, and societies of societies of societies" (Whitehead 1967, 206). Recent progress in physical chemistry has identified new modes of dynamic coherence (which occur in far-from equilibrium open systems) that are critically important in many areas of science—and have shown how those integrations exemplify and extend current theory (Kondepudi and Prigogine 1998). This major advance is not yet appreciated by philosophers—in part at least because such coherences do not easily fit into prevailing categorial schemes.

The world consists[19] of individuals that are composed of less-extensive components *and also* are parts of more-extensive[20] coherences. With appropriate technology, any item can be analyzed to yield stable materials—however those stable products of analysis need not have been components of the analyzed individual.[21] Similarly, It is possible to partition molecular electron-density distributions into atomic constituents (Bader 2011), but those hypothetical pieces are not the same as corresponding uncombined atoms would be (if such could be prepared).

Some philosophers hold that objects are nothing but aggregates (mereological sums) of their components. William Wimsatt (2006) carefully considered conditions under which such simple aggregativity may obtain—and found that those conditions are rarely fulfilled. Mereological summation does not apply when the functioning of two or more components either reinforce or oppose each other—but interactions of quarks in hadrons, hadrons in atomic nuclei, and electrons in atoms and molecules are all highly cooperative (as are actions of enzymes in metabolic networks, genes in organismic reproduction, social animals in hives and colonies, primates in their various groupings—including human societies). Classical extensional mereology is of vanishingly small relevance to any such examples of compound individuals. The usual case is that the spatial/temporal persistence of each object corresponds to a *closure of a network of relationships* among components (Earley 2013).

[17] Each emergent coherence corresponds to the closure of one or more networks of relationships—physical processes that have real consequences (Earley 2014, 2008).

[18] Chemists use the word 'substance' with a meaning different from the one used in philosophy—but usually do not notice that difference.

[19] The word 'entirely' is not appropriately used in the Searle quotation with which this paper begins, but it would be an appropriate modifier for 'consists' in this sentence.

[20] 'Extensive' has both spatial and temporal senses.

[21] Chemical analysis of samples of common salt yields metallic sodium and dichlorine (a noxious green gas)—but those stable materials are not in any sense 'components' of salt.

In order for important chemical and biochemical dynamic coherences to persist through time,[22] high-energy starting materials must enter (repeatedly or continuously) and products must leave (Earley 2006). Such higher-level coherences (called 'dissipative structures') result from *closure networks of relationship*s among dynamic components: those components include *processes* (such as chemical reactions) that destroy some items while producing yet others (Earley 2003, 2014). States of affairs that persist and/or recur are generally based on closure of networks of interactions among components.

Many-component systems are controlled by large (often immense) numbers of environmental variables (including concentrations of all components). If functions of components interact (either positively in catalysis of negatively in inhibition) systems will be unstable in some regions of parameter-space (Mainzer and Chua 2013). Such instability opens the way for the origin of more-extensive coherence through closure of networks of processes. The more complicated the original system is the greater is the probability of self-sustaining closure: if any such closure is possible, then generally myriads of mechanisms lead to self-sustaining closure (Kauffman 1993, 1995). In some well-studied chemical systems, molecular mechanisms of such effects can be elucidated in detail. Similar self-organization of dynamic open-system coherence also occurs in more-complex (e.g., biochemical, ecological, economic and political) situations for which molecular-level clarification is not to be expected.

William H. Sewell, Jr. (2005, 124 ff.) avoids explicit definition but understands *human social structures* as sets of habitual actions that persist or recur through a significant time-period—whether or not the human individuals involved are aware of those patterns or desire them to continue. This is analogous to the notion of dissipative structure in chemistry and evolutionary-stable-structure in evolutionary biology.[23] At least since the prehistoric origin of property ownership along with the beginnings of permanent human settlements (Renfrew 2009, 115 ff.) human social structures necessarily have involved some specialization of effort—differentiation of function—however small. According to Dewey, human individuality *originated* in such differentiation:

> To possess and exercise an *office* is to be representative and the history or development of offices, or representative functions, is the history of transformation of biological traits into traits constituting *persons*. . . . As in so many other cases, theoretical doctrine executes an inversion of actual order. Instead of moral relations existing because human beings are intrinsically persons, they become personal because of the rise and development of offices having at least rudimentary moral qualities. And this change from the biological to the distinctively human takes place not just under social conditions but *because* of influences, pressures, and commendations (approvals) occurring in group and community life. The case is similar to that in which, instead of acts being approved because they are virtuous in and of themselves, they become virtues because of the responses in others they habitually evoke. Just as men are worshipped not because they are gods but become gods because of the reverence and adoration which is accorded them. (Dewey 2012, 189–190)

[22] Such coherences cannot long persist in *closed* systems.

[23] This also has parallels in economics.

Arguably, development of human individuality made subsequent stages in cultural evolution more, rather than less, difficult—since individuals and groups would have sought to avoid the constraints of more-inclusive organizations (such as incipient states) when they could. Development of civilization required effective "caging" (Mann 1986) not just generating surplus resources.

6.11 Conclusion

The quotation of John Searle with which this paper started identifies an important problem for contemporary philosophy—but regrettably that quotation presupposes both stark dualism and 'un-modern' respect for the nominalistic presuppositions of current philosophy. An alternate version avoids the Cartesian bifurcation and suggests that clarifying the status of compound individuals—a main goal of philosophy of chemistry—is crucial to resolving Seale's conundrum. That alternative is: 'How is it possible, in a universe *analyzable into* physical particles and fields, that there *also are* atoms, molecules, dissipative structures, biological organisms, social structures, consciousness, intentionality, language, society, ethics, aesthetics, and political obligations?' Chemists interested in philosophy of chemistry can make crucial contributions to resolving the issue that Searle raises.[24] But, following Peirce at least this far, chemists should prefer intuitions that have been developed in their laboratories to the recommendations of academic philosophers.

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[24] And also the related objections brought up by Searle's critics, such as Thomas Nagel (2012).

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Chapter 7
One Substance or More?

Paul Needham

7.1 Introduction

The ancients disputed whether matter comprises a single or several substances, but by Aristotle's time several different substances were distinguished. Matter was then understood to be neither all of the same kind nor of continuously varying kinds, but as comprising particular substances that can be recognised as the same substance when we come across them on different occasions and in different circumstances. The identification of a particular substance among many therefore depends upon criteria of being the same substance. But picking out a particular substance in the first instance proceeds, we might think, without prior formulation of any such criteria, relying instead on a general criterion of being a single substance. Once we have our sample, we can then proceed to find characteristic features in terms of which criteria of being the same substance can be formulated.

Epistemologically, there may be something to the priority of the notion of being a single substance over the general relation of being the same substance. But the former is defined in terms of the latter, which is the logically prior notion. This is apparent from the approach of Aristotle, who took homogeneity to be the criterion of being a single substance. A quantity thus delimited by natural phase boundaries provides an observable sample which can then be studied for characteristic features. Portions of this can be investigated for properties, which might involve transformation into different substances, without loss of the entire original sample. The use of portions in this way is sanctioned by Aristotle's criterion of being a single substance since he maintained that all substances (elements and compounds) are homogeneous, or as he puts it, homoeomerous—comprise like parts: "if combination has taken place, the compound *must* be uniform—any part of

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such a compound is the same as the whole, just as any part of water is water" (*DG* I.10, 328[a]10f.). Here we see how the notion of sameness of substance comes in, a quantity of matter being a single substance if all its parts are of the same substance.

As understood above, portions of a sample are spatial parts (exhausting the matter occupying a region which is a proper part of the region occupied by the sample). Since Aristotle held that cooccupancy was impossible, the parts at issue in the passage just quoted were therefore considered to be spatial parts. After Aristotle, the Stoics thought of blends (at this time there was no generally recognised distinction between what we would call compounds and solutions) as comprising different elemental substances occupying the same place at the same time. Although many have followed Aristotle in denying the possibility of cooccupancy (albeit still unable to improve on Aristotle by offering an independent supporting argument), there is by no means a unanimous consensus on the issue.[1] If the possibility of cooccupancy is recognised, then the definition of being a single substance must be formulated with a restriction to spatial parts along the lines of: a quantity of matter is a single substance if all its spatial parts are of the same substance.[2] Identifying a single substance involves identifying a quantity all of whose spatial parts are the same substance.

Aristotle's criterion of being a single substance has long been abandoned in science, which for very good reasons distinguishes between substance and phase, allowing that a homogeneous quantity might contain several substances (e.g. a solution such as sea water or the air) and that a heterogeneous quantity might comprise a single substance (such as a mixture of ice and liquid water). Whether a quantity contains a single substance is not in general directly discernible by observation, even if the quantity of matter is. Chemistry has become more of a theoretical science as it has developed over the course of history and we would expect this to be reflected in its notion of substance, which has developed accordingly without preserving all its historical trappings. Whether different theoretical sources pull in the same direction, and in particular whether macroscopic and more recent microscopic perspectives are accommodated in a unified general picture, is not obvious, suggesting that the notion of a substance is not as straightforward as it might at first appear.

7.2 Thermodynamic Criteria of Sameness and Distinctness

A criterion of comprising a single substance should be general rather than varying from one substance to another, preferably based on an appropriate general theory. Aristotle's homogeneity criterion was general, but although part of an impressive theoretical stance in its time, cannot now be considered so. The notion of substance

[1] See Duhem (1892, pp. 271–273; 1893, p. 304; 1894, pp. 240–1), Tisza (1977), p. 128 and further remarks in this spirit in Needham (2007), pp. 41–2.

[2] For an explicit formulation of this and related principles governing the same substance relation, see Needham (ms).

is a macroscopic concept, but systematically distinguished from the concept of phase in what is currently accepted as the fundamental macroscopic theory, namely thermodynamics. This is a theory dealing with features of the world lying beyond the scope of mechanics that requires the division of the mass of a body into amounts of different substances composing it. We must resort to thermodynamics to explain how the mechanical phenomenon of pressure can arise by osmosis as well as how purely chemical phenomena involving change of substance lead to reaction equilibria. It is therefore natural to look for a general notion of substance governed by principles of sameness and distinctness of substance implicit in the theory. In particular, it is a natural place to look for systematic criteria based on the distinctive effects of the presence of several substances and of the special case of no more than one.

One such principle is the theorem of thermodynamics underlying Gibbs' discovery of the entropy mixing, which is independent of the nature of the substances, and in particular how similar they may be in any respect, but depends only on the amounts of the substances involved. The notion presupposes that the temperature and pressure, which would otherwise be sources of entropy change, are maintained throughout. A so-called ideal solution in which the components exhibit no interactive (attractive or repulsive) forces is one whose stability compared with that of the isolated components is entirely due to the entropy of mixing. The more similar the substances, the greater the difficulty in capitalising on this entropy difference in order to separate them (Denbigh and Denbigh 1985, Ch. 4). But the theoretical difference remains: mixing two quantities of the same substance doesn't increase the entropy, but any difference is marked by an entropy of mixing.

A more practicably applicable theorem is the phase rule, the first applications of which revealed many new substances where they were not suspected. The rule relates an experimentally ascertainable magnitude to the number, c, of substances in a quantity of matter and the number, f, of phases it exhibits, as follows:

$$\text{Variance } = c - f + 2 \geq 0.$$

The variance is the number of independent variables or degrees of freedom determining the state of the quantity. For a single substance, $f \leq 3$. Where there are three phases, the variance is zero and we speak of the substance at its triple point, a specific temperature and pressure at which the substance exhibits three phases. The usual situation is where the phases in question are solid, liquid and gas, which in the case of water occurs at 273.16 K (0.01 °C) and 611.72 Pa pressure (0.0060373 atm) and is used to fix a temperature above 0 K with which to calibrate the absolute (Kelvin) scale of temperature. Water also exhibits a number of distinct solid phases between which other triple points occur. Arbitrary small changes in temperature or pressure will convert the entire quantity of water at a triple point to one of the phases. The pressure of the ordinary triple point for water is the minimum pressure at which water can be liquid, so that in the low pressures of outer space, heating ice converts it directly to vapour. Here we see how the theoretical criterion of being a single substance points to sorts of properties that can serve as characteristic features of the substance.

The occurrence of two phases presents an experimentally more easily accessible range of behaviour. Here the phase rule specifies a variance of one for a single substance. A quantity exhibiting liquid and vapour in contact that can be kept at a fixed temperature in a closed container fitted with a piston has a pressure determined by the temperature (considered the independent variable). Thus, any attempt at increasing the pressure (by plunging the piston) at a fixed temperature is countered by material moving from the gas to the liquid phase. Similarly, attempting to decrease the pressure by raising the piston is countered by material moving from the liquid into the gas. Eventually, proceeding far enough in one direction or the other will lead to all the gas being converted to liquid or conversely, resulting in a single-phase system. Then the variance is two and temperature and pressure can vary independently (over a given range). But the volume is determined by these two variables (as in the ideal gas law), and cannot vary independently. This general behaviour is characteristic of a quantity of matter comprising a single substance, and the specific details of the functional dependencies of the pressure as a function of the temperature for the two-phase system is characteristic of the particular substance. In particular, the temperature at which the liquid changes into gas at a given pressure (the boiling point), like the vapour pressure at room temperature, are such details.

Identification of a new, hitherto unknown, substance by means of the phase rule doesn't necessarily require its isolation as a single substance. This is nicely illustrated by the way the demonstration of the phase rule soon led to the discovery of new, and previously unexpected, compounds. During the decade following the publication of Gibbs (1876–8), Roozeboom, aided by van der Waals' deductions, recognised that part of the phase diagram that he mapped out for the hydrogen bromide-water system was not the continuation of the vapour pressure curve of the then known hydrate $HBr \cdot 2H_2O$. It had a shape like that exhibited elsewhere in the phase diagram characteristic of a certain number of constituent substances but different specific features (values of the variables). It therefore corresponded to the presence of a new substance—a previously unknown monohydrate of hydrogen bromide (Wisniak 2003, pp. 425–6 relates the essential details). Previously established grounds for determining sameness and distinctness of substance had to accommodate the new contributions of thermodynamics.

The number of substances figuring in Gibbs' phase rule is notoriously the number of *independent* substances and not simply the number of substances. This arises because the derivation of the rule appeals to a number of general thermodynamic conditions connecting the intensive variables governing the thermodynamic state of the system, namely pressure, temperature and the chemical potential of each substance in each phase.[3] But the conditions obtaining in a

[3] In general, there is a connection between the chemical potentials of all the substances in a given phase given by the Gibbs-Duhem equation (f connections for f phases) and there are $c(f-1)$ interphase conditions given by the equality of the chemical potentials of each substance between any two phases. Thus, the variance $= 2 + cf - (f + c(f-1)) = c - f + 2$, the "2" deriving from the two intensive variables pressure and temperature (each having the same values for each phase).

particular case may give rise to further connections between the intensive variables, reducing the variance further. Thus, starting with n substances distributed over f phases, where there are additional conditions such as r independent chemical reactions coming to equilibrium and establishing connections between the chemical potentials, together with s stoichiometric constraints connecting the proportions of products of chemical reactions in a particular phase or several phases (these conditions may be intraphase relationships or interphase relationships), the variance $= n - f + 2 - r - s$. The number of independent substances, c, can be identified with $n - r - s$, but although this number is unique, which they are is usually not, and there are frequently several ways of selecting c independent substances from all those apparently present. However chosen, they may not all be present in all the phases, as assumed in textbook proofs such as that given here (footnote 3). Duhem (1898) pointed out that the well-known equilibrium established when calcium carbonate is heated in a closed container was such a case and proceeded to give a rigorous proof of the phase rule which doesn't rely on this assumption. Another case, studied by Zernike (1951, 1954), involves heating ammonium bicarbonate, NH_4HCO_3, in an initially otherwise empty container, when a dissociated vapour phase and a liquid phase appear in addition to solid ammonium bicarbonate. There is an *interphase* stoichiometric condition at play in this case, affecting the composition of several phases. The vapour phase contains ammonia, carbon dioxide and water, each of which have different solubilities in liquid ammonium bicarbonate. Consequently, neither the vapour phase (from which the substances dissolved in the liquid derive) nor the liquid has a composition corresponding to that represented by the formula NH_4HCO_3. The additional condition giving the proportions of the products of dissociation in the liquid and gas phases, which can be readily calculated, is counted as one of the conditions s that has to be taken into account in applying the phase rule. A further consideration is that enantiomorphs, usually counted different substances (see later), have the same values for their intensive properties except for rotatory power (equal in magnitude but opposite in sign). This may render some of the Gibbs-Duhem equations for different phases in a system no longer independent and therefore affect the variance (Scott 1977; Wheeler 1980).

The calcium carbonate equilibrium was one in which nineteenth-century scientists had to revise their apparent observation that only two phases—a white solid and a colourless gas—where involved because this wasn't consistent with a variance of one in the light of the phase rule. Usually the number of phases is a straightforward matter. But this still leaves several variables, often raising questions of interpretation which must be addressed before the number of substances present in a mixture can be determined from an application of the phase rule. Such interpretation usually calls on ideas about distinctions of substance drawn from other quarters. The microscopic realm is an obvious source, but as we will see, the idea of molecular structure is equally one which doesn't stand on its own feet. The notion of sameness of substance is an eclectic affair involving diverse theoretical inputs. A simple, unproblematic, universal criterion of sameness of substance is something of a pipedream.

The phase rule criterion of single substancehood is subject to restrictions, and even within its range of application, it conflicts with other criteria. It is restricted, first and foremost, to equilibrium conditions. Thermodynamics, and the phase rule deduced from it, applies to systems at equilibrium—that is, equilibrium under prevailing constraints (there is no unqualified notion of equilibrium). If a rigidly fixed wall of a vessel is somehow unlocked and allowed to move, for example, the system comprising the material in the vessel will readjust to the new equilibrium conditions, perhaps by reducing its internal pressure or changing the amounts of matter in two or more phases. The question of how to recognise equilibrium is a notorious issue. Duhem was led to introduce the notion of false equilibrium for apparently unchanging states which don't comply with thermodynamic conditions. Clearly, it is not a simple matter of observation, as Callen puts it in his well-known textbook:

> quiescence is not sufficient. As the state is assumed to be characterised completely by the extensive parameters, $U, V, N_1, \ldots, N_r$, it follows that the properties of the system must be independent of the past history. This is hardly an operational prescription for the recognition of an equilibrium state … In practice the criterion for equilibrium is circular. *Operationally, a system is in an equilibrium state if its properties are consistently described by thermodynamic theory!* (Callen 1985, pp. 13–5)

Callen illustrates the point by pointing out that "failure of H_2 to satisfy certain thermodynamic equations motivated the investigations of the ortho- and para-forms of H_2" (loc. cit.). Whether concepts applicable under equilibrium conditions continue to apply under non-equilibrium conditions calls for careful consideration. Temperature, for example, is a thermodynamic concept not applicable to a body which is not at equilibrium. But an extension of thermodynamics to irreversible thermodynamics allows that, under not too radical non-equilibrium conditions, thermodynamic concepts such as temperature can be applied to points at instants of time, varying smoothly from one point and time to another.[4] In that case, even though a body not at equilibrium doesn't have a temperature, it may well be possible to assign a temperature gradient over the body. A similar distribution of substances may be possible throughout a body subject to diffusion and chemical reactions.

A related constraint concerns the time scale of the intervals during which two quantities stand in the same substance relation. Thermodynamic equilibrium corresponds on the microscale to a dynamic balance between constantly ongoing processes, which is achieved for times long enough for fluctuations to be ironed out by statistical averaging. It can therefore only provide criteria for sameness and distinctness of substances holding for sufficiently long times. This covers intervals

[4] It is apposite to note that in his final chapter, Denbigh (1981) emphasises the importance of the concept of equilibrium even in kinetics: "There is no theory of rates which stands … on its own feet; all existing theories depend, in one form or another, on ideas carried over from the study of matter at equilibrium" (p. 439).

short on a human time scale down to a microsecond and less; more precise specification of a lower bound depends on the circumstances.

Another kind of restriction is imposed by the range of conditions over which the substance is stable. The determination of melting and boiling points which had become such a well-established method of characterising substances in nineteenth century organic chemistry was not applicable to biologically active substances such as proteins, which decompose on heating before changing phase. But by the time proteins were recognised as comprising macromolecules—much larger than anything envisaged by chemists in the first decades of the twentieth century (Zandvoort 1988; Furukawa 1998)—other methods of identification had been developed. Throughout much of the twentieth century, substances have been identified by their distinctive spectra. Although spectra have been subjected to thorough analysis concerning the origin of their specific features in aspects of molecular structure, they have also served as unanalysed characteristic marks in much the same way that colour, smell, consistency, melting point and boiling point were used in the past. Characteristics criteria of this sort can serve to classify distinct quantities of matter as the same substance at the same time or one or more quantities as the same substance at different times.

7.3 Comparison and Conflict Between Macro- and Microscopic Criteria

Other criteria of being a single substance and sameness of substance are called upon in circumstances like those mentioned when the thermodynamic criteria are inapplicable. Though motivated by different considerations, these may sometimes be applicable under the same conditions that thermodynamic criteria are. A natural expectation might be that such overlapping criteria would agree where both are applicable, so that they may be taken to complement one another in the cases where one is not applicable. Unfortunately, the situation is not so rosy.

An example is the isotopic variants of substances. According to the IUPAC ruling, atomic number determines sameness of element kind (Aston et al. 1923, p. 868). Previously, atomic weight had been taken to be characteristic of an element. But the discovery of isotopes led to a situation in which elements with different atomic weights were assigned the same position in the periodic table on the strength of their "chemical" properties. Differences in the "physical" properties of isotopes assigned the same position in the periodic table were usually small. These are the mass-dependent properties such as solubility (expressed in grams per unit volume rather than moles), specific gravity and properties depending on intramolecular vibrations such as specific heat and the elastic properties of solids. The glaring exception was radioactivity. Among groups of isotopes assigned the same position in the periodic table, some were radioactive and others were not. Faced with the collapse of the systematisation of the elements introduced by the

periodic table that would follow if atomic weight continued to be used to characterise elements, the IUPAC introduced its ruling in 1923 that the elements were to be characterised by atomic number rather than atomic weight. This was justified in terms of the increasing understanding of the way the chemical properties of an element are related to the electronic configuration of the isolated atom, which is in turn governed by the number of protons in the nucleus, i.e. the atomic number. The ruling on elements would carry over to their compounds, whose properties play an important part in characterising positions in the periodic table, so that isotopic variants of compounds with different isotopes of a given element are counted the same substance.[5]

The 1923 IUPAC ruling followed Paneth's recommendation, which had been challenged by Fajans in a debate leading up to the ruling. One of Fajans' points built on a thought experiment of Polanyi's suggesting that the spontaneous mixing of isotopes is accompanied by a decrease in the Helmholtz free energy because the process is irreversible, accompanied by an entropy of mixing (van der Vet 1979, pp. 294–5). In a comprehensive review and assessment of the Paneth-Fajans debate, van der Vet (1987, Ch. II) argues that the thought experiment is mistaken. The work is performed by the gravitational field, and in general, the entropy of mixing cannot lead to observable effects providing a test of difference because any work done in separation would be due to intermolecular interactions, whereas the entropy of mixing is independent of any such interactions (pp. 116–8). Polanyi's thought experiment inspired "an incorrect argument ... instrumental in the introduction into the debate of a point accepted as correct today, namely that isotopes are thermodynamically different" (p. 63). For example, there is an inequality of proportions of isotopes in contiguous phases at equilibrium, which is large enough in the case of hydrogen isotopes to allow separation by electrolysis.

When the distinction between physical and chemical properties was still a live issue, it may have seemed that distinctions of *chemical* substance should rely on the atomic number criterion and overrule thermodynamic distinctions of substances. This is already a controversial claim in relegating thermodynamics to the study of physical properties. But since 1923 it has become possible to discern differences in the kinetics of chemical reactions arising from isotopic differences. The effect is most marked in the case of hydrogen isotopes, as a result of which heavy water (unknown in 1923) is poisonous—a classical chemical difference if ever there was one! Of course, the differences are small and for many purposes may be ignored, as in other cases (e.g. straight-chain alkanes of high molecular weight) where the similarity is so great as to be of little consequence. But that doesn't detract from the fact that there is, in principle, a distinction of substance to be made (Needham 2008a). This is not to deny that the more fine-grained criterion "was not part of the intellectual context that informed earlier thinking about the elements" (Hendry 2010, p. 927) in the pioneering studies of the periodic table. But the question is

[5] Isotopes of oxygen might all be called oxygen just as isomers of heptane might all be called heptane. The substantial point is whether isotopes are counted different substances as isomers are.

how to view the matter now that we are aware of the chemical differences. These differences fall off rapidly with atomic number, and for many purposes are negligibly small. But where precision is at issue, ignoring the kinetic effects of variation in atomic weight is to ignore subtle differences in chemical features of the reactivity of compounds. This is sufficient to count isotopic variants different substances, however subtle the difference, by taking into consideration subtleties of which chemists of bygone eras were unaware.

The elemental composition of a compound only settles its compositional formula. Berzelius was led to coin the term "isomer" in the 1820s for a different substance with the same compositional formula. Differences that first came to the attention of chemists were chemical—dimethyl ether, $(CH_3)_2O$, is much less reactive than ethyl alcohol, CH_3CH_2OH, with the same compositional formula, C_2H_6O—accompanied with differences in physical properties such as melting and boiling points. The notion of a structural formula was elaborated as a topological structure indicating which elements are linked to which as a finer development of compositional formulas serving to represent distinct isomers. They were seen as structures derived from an archetypical compound by substitution. Thus, alcohols were derived from an equivalent of water by the substitution of a(n equivalent of) hydrogen by an alkyl group (C_nH_{n+1}) and were said to be of the water type. Williamson famously showed in 1851 that ethers could be regarded as water in which two equivalents of hydrogen are replaced by alkyl groups, which need not necessarily be the same. At the same time this settled the compositional formula of water as H_2O, rather than, for example, HO as Dalton maintained.

Later in the century pairs of substances turned up which seemed to be alike chemically but differed in one or two physical properties. They might form crystals whose shapes are mirror images of one another, or they might form solutions which rotate the plane of plane polarised light by equal amounts in opposite directions. These were stereoisomers, calling for more developed structural formulas displaying the orientation of elements to one another in three-dimensional space and differing in the one being a mirror image of the other. Internally they were alike. Chemical reactions were subsequently discovered that are stereospecific, where a given stereoisomer will only react with a specific stereoisomer of the other reactant. This is generally the case with biochemically important reactions, where the naturally occurring form of one of the reactants is a specific stereoisomer that will only react with specific stereoisomeric forms of the other reactants.

Evidence of chirality, then, is a mark of distinction between substances. This provides another reason in support of the thesis that isotopic variants are distinct substances in conflict with the 1923 IUPAC ruling. Kokke and Oossterhoff (1972, 1973), for example, have shown that substitution of oxygen-18 for the more common oxygen-16 isotope in an optically inactive compound gives rise to chiral effects. The substitution of deuterium for protium gives rise to a similar but more marked chiral effect.

For much of its history, the theory of structural formulas could be developed without recourse to the atomic theory (Duhem 1902; Needham 2008b). But the reality of the microworld was convincingly established at the beginning of the

twentieth century, after which structural formulas have been interpreted as depicting molecules (an idea completely foreign to Dalton's conception of microstructure, which included no notion of entities comprising small numbers of interlinked atoms not so linked with neighbouring atoms). From such beginnings there arises the *molecular structure thesis*, according to which a quantity of a single substance is a collection of molecules of a single kind and sameness of substance is governed by sameness of molecular structure. But this microscopic criterion faces several challenges.

Although molecular structure thesis is straightforwardly applicable to a range of organic compounds, many substances are not molecular. The silicon dioxide in a grain of sand is not divided into SiO_2 molecules, but a covalently bonded structure extends over the whole grain. Similarly, an ordinary ionic compound like common salt comprises uniformly distributed ions, not NaCl molecules (a conclusion still disputed in the late 1920s[6]). However, broadening the general thesis by more carefully specifying "molecular structure" in different ways to accommodate many less straightforward cases raises the danger of conflict. Thus, for many substances which, unlike typical organic compounds, are not molecular in the sense that quantities of them are collections of molecules of a single kind, it would appear that the molecular structure thesis would have to count as many substances as there are different molecular structures, contrary to normal practice based on other criteria. Other substances apparently call for further specification of structural features beyond what is needed to distinguish stereoisomers, and this can lead to conflict with what is said in the case of non-molecular substances. Water and proteins illustrate these points nicely.

Water is the notorious example of a non-molecular substance which is particularly complicated in the liquid phase. Intramolecular bonds are constantly being broken and reformed with the creation and recombination of hydrogen and hydroxyl ions whilst intermolecular hydrogen bonds forming polymeric species form and break incessantly. Consequently, a given quantity of water cannot be mereologically partitioned into simple H_2O molecules for any given time but comprises entities considerably larger than an H_2O molecule whose parts are constantly severed and rejoined in new constellations. Nevertheless, it is a single substance by the phase-law criterion. But it is difficult to see how the molecular structure thesis could agree with this ruling, although it is equally unclear how many substances it would rule that there are in a glass of water at normal temperature and pressure during a given time.[7]

[6] Armstrong (1927, p. 478) regarded Bragg's claim that in sodium chloride there are "no molecules represented by NaCl. The equality in number of sodium and chlorine atoms is arrived at by a chessboard pattern of these atoms; it is a result of geometry and not of a pairing-off of the atoms" as "repugnant to common sense" and "not chemical cricket".

[7] I suggest that the macroscopic quantities to which the two-place predicate applies for macroscopic intervals of time are structureless mereological sums of all the material bits that partake of these interconversions at the microlevel (Needham 2010b).

The analysis of protein structure at the molecular level tells us that structural features sufficient to characterise and distinguish the kinds of organic compounds studied in the nineteenth century, such as the topological ordering of bonded atoms and the geometric orientation of bonded atoms about a given atom, would seem insufficient to characterise proteins. When denatured, by gentle heating or subjecting to low pH conditions, proteins loose their biologically relevant chemical properties and become biologically inert, although the underlying pattern of covalent bonding—the so-called primary structure—that would serve to characterise many organic compounds is preserved. What is lost is their secondary and tertiary structure, characteristic of the way long chains fold back on themselves and are held in place by weak hydrogen bonds, which is correlated with chemical reactivity of the kind traditionally taken to be characteristic of a substance. It seems that the loss of chemical reactivity compels us to take secondary and tertiary structure to be essential features of the characteristic molecular structure. Merely considering which atoms are covalently bonded to which and how the bonds are oriented in space would count proteins in the natural and denatured states at the same temperature and pressure as the same substance, despite a considerable difference in chemical reactivity. But taking similar account of hydrogen bonding in water would lead us to consider it a mixture with continually varying composition.

Intermolecular interactions are always present, raising the question of when they contribute to determining the structure of the substance-determining microentity in accordance with the molecular structure thesis and when not. Equimolar mixtures of stereo enantiomers are racemic, with zero net optical rotation. Some form separate (+)- and (–)-rotatory crystals when they crystallise, in which case the mixture is a mechanical mixture displaying a melting-point diagram (plotting melting temperature against composition) typical of mixtures. The melting point of either pure form is lowered by addition of the other, reaching a minimum (eutectic point) at the 50:50 % composition. But some racemates crystallise as a single racemic compound, acting as a compound distinct from either enantiomer and displaying a peak in the melting point diagram at the 50:50 % composition point. Addition of the (+) form lowers its melting point until a eutectic point is reached, and addition of the (–) form similarly lowers its melting point until another eutectic point is reached. The IR spectrum of solid racemic compounds also differ from the enantiomers (Eliel 1962, pp. 43–7). The presence of two distinct molecular structures is therefore not sufficient to determine whether there are one or two substances present. A thermodynamic criterion determines whether the 50:50 % composition point corresponds to a single substance, a racemic compound, or a mixture.

Questions about the individuation of the relevant molecular entity also arise because molecular structure is not a static feature. Molecular geometry is in reality constantly changing within certain limits as bond angles and lengths change in vibrational modes and because of distortion due to rotation. The threat of a single molecular structure giving way to an indefinite number of varieties is avoided, it seems, by resorting to tabulated values of bond angles and lengths understood as

time averages over these continuous variations. Sameness of molecular kind would then presuppose a time scale appropriate to this averaging so that even from the microscopic perspective, substance concepts don't apply for arbitrarily short times. But there are complications. According to this notion, methane is a paradigmatically symmetric molecule with a tetrahedral structure and no chiral features. But there is a small but measurable dipole moment in the vibrational ground state due to rotational motion, which reduces the molecular tetrahedral symmetry to axial symmetry, as a result of which molecules rotating in the same sense as the electric vector of light differ in polarisability from molecules rotating in the counter direction. The difference is small, but not beyond the limits of measurement. Consequently, "ordinary methane is properly regarded as optically inactive not because of the intrinsic inactivity of the molecules but because it is an enantiomeric mixture" (Atkins and Gomes 1976, p. 519). The substance is not optically inactive because the molecules are all the same, but because of the distribution of different kinds of molecules. The perfect geometric structures captured by time averages are not quite the structures of real molecules even for appropriately long intervals of time.

The averaging process at issue in this last example brings to the fore the significance of the amount of material. The notion of substance is a macroscopic concept, applicable to macroscopic quantities. A microscopic criterion of substancehood would be one applicable to a sufficiently large collection of microentities. Mislow and Bickart (1977), p. 2 characterise "ensembles of achiral molecules [whose properties] result from statistical cancellations of local chiral effects" as stochastically achiral, and go on to extend the notion to include systems at equilibrium consisting of chiral molecules which rapidly enantiomerise on the time scale of observation. Above –230 °C, for example, the distinction between the two gauche conformations of butane is lost when thermal motion is sufficient to overcome rotational barriers and the enantiomers interconvert, but below this temperature the conformers apparently constitute two different substances. Absence of measurable chirality doesn't, however, imply stochastic achirality. Quoting from a 1932 article of W. H. Mills, Mislow and Bickart (1977), p. 3 note that "when 10,000,000 dissymmetric molecules are produced under conditions which favour neither enantiomorph, there is an even chance that the product will contain an excess of more than 0.021 % of one enantiomorph or the other. It is practically impossible for the product to be absolutely optically inactive". Moreover, as percentage excess decreases with increasing size of sample, the number of molecules in excess increases and along with it the probability of obtaining a strictly racemic sample decreases. Such deviations from achirality may be beyond the powers of our observational resources, but their occurrence is ubiquitous. Thus, the actual molecular composition of macroscopic quantities of matter may be complex, depriving us of a simple rule relating number of substances and molecular structure. An apparently optically inactive mixture needn't be a 50:50 mixture of corresponding enantiomers, and a 50:50 mixture of corresponding enantiomers might be a single substance, not two.

7.4 Concluding Comments

Like temperature, the notion of a chemical substance is a macroscopic notion which resists reduction to purely microscopic notions. The familiar idea that gas temperature is the average kinetic energy of the constitutive molecules does not amount to a reduction because temperature presupposes equilibrium, the microscopic correlate of which is the Boltzmann distribution and this in turn presupposes the macroscopic notion of temperature (Needham 2009, 2010a). Similarly, any quantity of matter characterised as being a particular kind of substance will have microscopic features, yet it doesn't follow that the macroscopic notion of substance is reducible to microstructure. The reason is less straightforward than in the case of temperature, but of essentially the same kind. If having particular microscopic features, such as comprising a particular kind molecule, provided an adequate general criterion of being a single substance, where the microscopic features can be independently specified (i.e. without reference to the substance in question), matters would be different. But as matters actually stand, substances are not in general of a microscopic kind such as being molecular, i.e. comprised of numerous microscopic entities of a single kind. Molecules are microscopic entities themselves composed of entities of several kinds (electrons, protons and neutrons) combined in such a way that they move as a single, integral unit, and not merely minimal units corresponding to a compositional formula like SiO_2 or NaCl which do not comprise internally bound parts not so bound to other immediate neighbours. ("The smallest part of a chemical compound that can take part in a chemical reaction" sometimes offered as a definition of a molecule calls for immediate qualification (Daintith 1990, p. 195) because it encompasses much more, capturing instead this broader notion of a minimal unit.) Although there are many molecular substances, comprised of millions of molecules—in this sense—of the same kind, the fact that many substances are not molecular entails that comprising a particular kind of molecule is not an adequate general criterion of being a single substance.

The concept of a chemical substance is more complicated, then, than a simple molecular structure thesis would have it. The assumption that there is a single kind of molecule collections of which constitute samples of a corresponding substance must give way to an *explicit specification* of any microstructural description that is held to correspond to a particular substance. It is almost a tautology that a substance has that substance's microstructure, not quite because of the existential presupposition, which received its empirical justification with Perrin's investigations into Brownian motion and the general recognition of a discrete microstructure underlying an apparently continuous macrostructure. But this is such commonplace knowledge that it goes without saying, and just as Perrin's investigations told us almost nothing about the chemical nature of microstructure, so "water has the microstructure it has" and essentially equivalent variants say practically nothing. A microstructural account of a substance, i.e. what being the same substance as the particular substance amounts to, can only be a detailed explicit specification of the microstructure. The question is whether such specifications are independent of

macroscopic considerations while sufficiently accurate to entail the macroscopic properties. Despite all the work that has been put into elucidating the microstructure of water, a sufficiently accurate description facilitating the deduction of thermodynamic properties still eludes us.

I have tried to say something about how micro- and macrocriteria for being a single substance and the same substance work together. The dominating idea has been that the notion of substance is one that applies to macroscopic quantities of matter for macroscopic intervals of time. Questions arise about the precise lower limits of these magnitudes and whether a single, universal criterion of sameness settling all questions will emerge. This conception might be criticised for not including recently reported transuranium elements whose discovery has been claimed on the strength of the fleeting existence of no more than a few atoms. Polymers might also be seen as threatening the conception of substance, where features of the mixture of molecular kinds, such as the distribution of chain length, are controlled for optimal properties of the macroscopic quantities of material and the question of sameness of substance becomes irrelevant. Shorted-lived reaction intermediates and transition states aren't around long enough for what is true of macroscopic intervals of time to apply. Clearly, the notion of substance is not the chemist's only concern, and it has not been my intention to suggest otherwise. I only claim that it continues to be an important concern.

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Chapter 8
Mereological Principles and Chemical Affordances

Rom Harré

Mereology, the logic of propositional reasoning concerning relations between wholes and parts, has always been important in philosophy of chemistry, though for the most part as a set of unexamined tacit principles. Mereological rules have shaped chemical theory, particularly where it has been concerned with the constitution or nature of material substances. Recently studies devoted explicitly to mereological principles as they are relevant to chemistry have been published in the writings of Paul Needham (2005), Joseph Earley (2005) and Jean-Pierre Llored and Rom Harré (2011).

However, the logic of reasoning about parts and wholes and the fallacies to which such reasoning can be subject is much advanced by drawing the concept of 'affordance' into the discussion. The neologism 'affordance' was coined by the psychologist J. J. Gibson (1979) to refer to the content of a sensory impression. We see that a sharp knife affords cutting rather than inferring its capabilities from a physical measurement. We see that a floor affords walking without carrying out tests. However, the affordances of something are relative both to the way it is interacted with and to the context in which an interaction takes place. In terms of familiar logical concepts affordances are a species of disposition for which the actor and that which is acted upon are the indissoluble components of the being that is characterized by this or that affordance. Chemists and other scientists can be seen as engaged in finding out a slice of the gamut of affordances which specific apparatus-reagent complexes display. In what follows I will show how thinking in terms of parts and wholes can be elaborated and clarified by seeing chemistry as the study of affordances.

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8.1 Historical Sketch of the Advent of Chemistry as a Mereological Science

Robert Boyle (1661) set the shape of chemistry for centuries with his mereological principles which encapsulated his corpuscularian philosophy. The generic principle, that chemistry is based on considering material stuff to be composed of minute parts, appears at the very beginning of *The Sceptical Chymist*. '. . . that which we discover partly by our *Microscopes* of the extreme littleness of even the scarce visible parts of Concretes and partly by Chymical Resolution of mixt bodies, and by diverse other operations of Spagyrical Fires upon them, seems sufficiently to manifest their consisting of parts very minute and of differing figures . . .' (Boyle 1661: The First Part, Prop 1).

The presumption that the salient properties of the invisible corpuscles are the same as the visible parts extracted by various processes is represented in his *The Origin of Forms and Qualities according to the Corpuscular Philosophy* (Boyle 2nd Edition 1667: i). There he makes clear the presumption of all corpuscularian science that the relevant properties are the 'bulk, figure, texture and motion of the insensible parts'.

> What I am chiefly aiming at is to make it probable to you by experiments. . . .that almost all sorts of qualities—most of which the schools have either left unexplained or else 'explained' in terms of I-know-not-what incomprehensible 'substantial forms'—can be produced mechanically. I mean: they can be produced by corporeal agents that seem (**a**) to work purely by virtue of the motion, size, shape, and inner structure of their own parts (I call these attributes 'mechanical' affections of matter because they are what we willingly turn to when explaining the various operations of mechanical engines), and (**b**) to produce the new qualities exhibited by the bodies they act on purely by changing the texture, or motion, or some other mechanical affection of the bodies in question. (Boyle 1667. Preface p. 9)

Whether or not there were indivisible corpuscles, 'atoms', did not affect the way Boyle's mereology was developed over the next two centuries. For example, Dalton presented the metaphysical foundation of chemistry as an atomic theory. Boyle was explicit in his cautious approach to attributing ultimate indivisibility to the units of chemical reactions.

Considering material substances to be clusters of parts is the bare minimum for a mereology for chemistry. Specific applications of the rules for part-whole reasoning depend on the relation between the properties of the whole and the properties of its parts. For example, in Boyle's chemical metaphysics the corpuscular constituents of material stuffs have some of the same properties as the materials of which they are parts. Which properties are shared between parts and wholes is a fundamental aspect of chemistry at any one historical moment. For example, restrictions on which predicates could be transferred down a chain of inferences from parts to wholes and wholes to parts were expressed in the distinction between primary and secondary qualities, as formulated for example by John Locke (1689: Bk II, Chapter 8, Section 23). Colour, taste and other 'secondary' properties were not transferred from wholes to their parts. Wholes and their parts shared 'mechanical'

properties, such as ‘shape’ and ‘bulk’. The beginnings of gravimetric analysis in the late eighteenth century required an additional shared property. The weight of a whole was a sum of the weights of the parts. So, the possibility of determining ‘atomic weight’ became thinkable. As this principle was refined by the distinction between ‘weight’ and ‘mass’ the two main mereological principles retained their dominance. The properties of a whole were some function of the properties of the parts, and the products of analysis of such wholes were constituents of the original wholes. The reasoning from experimental results to atomic weights and the use of the results of Aston’s mass spectrograph to identity elements depended on these basic mereological rules, as did many other chemical methods and theories.[1]

8.2 The Mereological Core of Chemical Thinking

Thinking in terms of wholes and their parts draws attention to several distinctions of importance in chemistry.

(a) Kinds of wholes: Structural wholes consist of a collection of stable elementary parts held together by at least some invariant relations, e.g. molecules, organic and inorganic; dissipative wholes consist of bounded and stable array of processes the material of which flows into and out of the system, e.g. flames, smelting hearths (Earley 2005).
(b) Kinds of constituents: those which retain their identity when detached from the whole of which they are parts, e.g. molecules, atoms (ions), some organic radicals; those the identity criteria of which change when detached from the wholes in which they were parts, e.g.

In addition to the part/whole thinking that is the basis of the atomic theory in chemistry there is also the way mass concepts, such as ‘water’, ‘gold’ and so on are managed. Mass terms refer to extended substances which can be split into parts which share those properties of the wholes from which they come that identified them as substances. A gold ring is as much gold as the ingot from which it came. A version of the basic mereology is involved in this domain too. To lay out the principles of the mereology of mass substances Needham (2005) uses a distributive condition that requires that each part of a mass substance is an instance of that mass substance, and a cumulative condition, that the fusion of instances of a mass substance is an instance of that mass substance.

These ‘conditions’ are similar to those of the corpuscularian mereology except that the size, shape and mass of the ‘parts’ of mass substances are created by the choice of the means by which parts are produced. The identity conditions for parts and wholes of mass substances are contingent on choice of ‘bucket’.

[1] I will take the expression ‘atom-core’ from Joseph Earley’s writings to cover free ions as well as atoms in situ in stable molecular structures.

8.3 The Basic Principles of Mereology

To explain and make plausible the principles of mereology for the thinking in any disciple one could illustrate their meaning by setting out a range of examples of their use in making sense of the phenomena in a certain domain. However, since the early part of the twentieth century it has become popular to try to express such principles in terms of some well-established formal system. The system of choice for displaying mereological principles, such as those enunciated by Stanislaw Lesniewski, as presented by Srzednicki and Rickey (1984) has been set theory.

Lewis (1991: 1) proposes the term 'fusion' for any whole composed of some parts.

> There is a unique being which is the *fusion* of a collection of beings which consists of only these beings. For example a particular chemical molecule is such a being.

He notes that these parts might be atomic or they might be arbitrary bits of some sort of 'atomless gunk'. As we will see mereology in chemical thinking has made use of both. This definition expresses the way that certain collections of atom-cores behave as individuals and so can be considered parts of higher order entities. Water molecules, in the commonest aqueous form of H_2O, are fusions of hydrogen and oxygen atom-cores and as such are parts of lakes and oceans.

The basic steps to a formal treatment of mereology were taken by Stanislaw Lesniewski's mereology (Srzednicki and Rickey 1984) is a basic system of rules for valid reasoning about wholes and their parts. David Lewis carried through the mapping of intuitive mereological rules onto the formal system of set theory. To do so he began with two definitions (1991: 73).

D1: X and Y *overlap* if and only if they have some common part. If and only if not, they are entirely distinct.
D2: Something is a *fusion* of some things if and only if it has all of them as parts and has no part that is distinct from each of them.

From these definitions we can derive the notion of 'part'. 'X is a *part* of Y if and only if everything that overlaps X also overlaps Y'.

Lewis's axiom for mereology are similar to the original proposals of Lesniewski.

Axiom 1 Mereological transitivity: If X is a part of some part of Y and then X is a part of Y.

The concept of 'radical' as a unit such as NH^3 plays a similar role to an atom-core in the constitution of a molecule such as ammonium chloride. By mereological transitivity the hydrogen atom-core which is part of the radical is also part of the molecule and is treated as such in its many roles in chemistry.

Lewis added two more axioms: 'whenever there are some things, then there exists a fusion of those things' and 'it never happens that the same things have two different fusions'. These axioms seem to be a poor fit to the way chemical wholes are fusions. They do not distinguish between structured wholes such as ammonia molecules and mass wholes such as ammonia gas. How do we incorporate enantiomorphic sugars into the scheme? It seems that structure is an ineliminable

aspect of how the part-whole relation is applied in chemistry. In that respect its interpretation as a branch of set theory is not rich enough for the job.

Taking a one membered set as an individual in this system a comprehensive mereology can be devised provided that the sets involved do not differ one from another by internal structures. For example Lewis ties sets to parts with the principle 'One class is part of another if and only if the first is a subclass of the second'. So, in chemical terms, an atom is a single membered subset of the set of atoms that is the relevant molecule, and so on. However Lewis notices that there is a kind of disparity between a singleton as a one-membered set and as a distinct individual. He asks how does a single item form a class when the notion of 'class' is introduced as the elements that are *gathered together* as a class. If the concept is entirely formal this issue seems irrelevant. Taken formally mereology does not deal with unique individuals, that is any one for which there *could* not be another like it.

8.4 Limits to Part-Whole and Whole-Part inferences

Mereological reasoning, so central to the formation of well-ordered chemical discourses, is vulnerable in certain circumstances to its own brand of fallacies. There are two fallacies involving inferences between claims about wholes and their parts. It is a fallacy to ascribe an attribute the meaning of which is determined by its use for a whole to a part of that whole (though not in every case). It is a fallacy to take the parts of a whole to be constituents of the unanalyzed whole from which they came (though not in every case). Is there a systematic way of deciding in which cases there is the threat of a mereological fallacy and in which cases projecting attributes from wholes to their parts and treating products of the analysis of wholes as constituents of those wholes is acceptable?

Distinguishing between primary and secondary qualities, as Boyle and Locke did, is one principled way to make this distinction, but is there a more general rule for licensing and forbidding transfers of properties from parts to whole and whole to parts? A clue to how this question could be answered can be found in the way mereological fallacies haunt psychology, particularly neuroscience.

The first mereological fallacy is exemplified by a prevalent error in neuropsychology (Bennett and Hacker 2003). It is an error to ascribe an attribute which gets its meaning from its use to characterize a whole human being to a part of that human being. Thus, to say 'the frontal lobes make decisions' is a mereological fallacy because the word 'decide' gets its meaning as something a whole person does. A drag racer can accelerate at a metres per second per second, but none of its detached parts can. The acceleration they are subject to as parts of the assembled racer can be attributed to each of them only in so far as they are integrated into the car. 'Acceleration' is a concept that gets its meaning in this context from its use to describe the motion of a whole car.

The second mereological fallacy threatens when it is taken for granted that the products of an analytical procedure exercised on a whole can be read back into that whole as its parts or some of its parts. In psychology one can elicit memories from another person of past tense statements or depictions of the past but it is a fallacy to assume that such discrete memories are components of the person who has expressed them. This fallacy appears in the concept of the memory 'store' and the concept of an 'engram'. Whatever it is that grounds a person's capacity to remember things it is not a box full of 'memories'. The discrete components of a living human being that make remembering possible are the molecular structures of neural nets. The attributes that make a recollection this memory are quite different from those make a molecular structure this engram.

To disentangle the conditions under which the fallacies occur another important concept has recently been added to the philosophical repertoire for analyzing chemical discourses. This is the concept of 'affordance'.

8.5 Affordances

'Affordance' is the word coined by J. J. Gibson (1979) to present his theory of perception. This was a radical departure from the sense data theories of such as Russell and the constructionism of such as Kant. In those theories what we see is said to be the product of a cognitive process by which elementary sensations, such as coloured patches in the visual field, are synthetized into objects and processes. Gibson argued that certain invariant structural properties of things afforded perceptions of those things to people and animals as they explored the flux of electromagnetic and sonic energy within they lived. Not only that, but Gibson pointed out that we can also discern perceptually what something can be used for. Most people can see that a knife can be used for cutting – in this terminology we say a knife affords cutting. But only in a human context does a certain piece of steel have that attribute. We can also say that a floor affords walking to people, while a lake does not, though it did to Jesus. An affordance is relative to context, in particular to the specific interaction between some human beings and the material world.

From the point of view of the grammar of a chemical discourse an affordance is a disposition or capacity as ascribed to a certain material being to yield an observable effect when acted upon in a certain manner. It may be an observable property, say 'tensile strength', or an entity, say a gas as the product of a chemical reaction, that is when certain substances are acted on in a certain way. In mereological chemistry we conclude that the advent of tensile strength is due to a new arrangement of the atoms in the molecules of at least one of the reagents, while the advent of the gas is the release of a constituent of one of the original substances. We imbibe mereological thinking with the very first chemical experiment many of us perform – obtaining a sample of hydrogen from the reaction of metallic zinc with a dilute solution of hydrochloric acid.

Written out in full the attribution of an affordance has the form of a conditional – 'if a certain procedure is carried out on a certain substance then it will display a certain attribute or yield a certain substance'. So adding carbon to iron increases the tensile strength of a rod, that is a property it displays only when put into tension in some machine. Adding zinc to a solution of hydrochloric acid yields a gas that after several decades of eighteenth and nineteenth century debate we now label 'hydrogen'. Hydrochloric acid affords hydrogen only in certain particular circumstances.

8.5.1 Categories of Affordances

The pattern in which the second mereological fallacy can infect the validity of reasoning in chemistry appears in the inferences we are inclined to make linking the results or products of analytical processes to the material stuffs from which they were derived. The methodological question is whether the products of an analytical procedure were constituents of the being on which the process was exercised. In the root procedures in chemistry do we have analysis of things into their parts or the genesis new beings? To assume that analytical processes directed towards targets *always* yield constituents is to fall into the 'product-process' fallacy, or the second mereological fallacy. The concept of 'affordance' can throw light on how this fallacy comes about and in what circumstances. It is not a fallacy to draw inferences about the molecular weight of a certain compound from knowledge of the atomic weights of the products of its analysis.

1. Affordances as substances – things and stuffs – for example, distillation affords alcohol. There was alcohol in the liquor before it was separated out, so to say that alcohol was a constituent of the liquor is a valid inference. Electrolysis of silver nitrate solution yields silver ions, so to say that silver atom-cores were parts of the solution is a valid inference.
2. Affordances as attributes – properties – for example, heating a solid affords liquidity; passing light through a prism affords a spectrum of colours on a white surface. Was liquidity a hidden property of the solid? Surely not. But Newton realised that coloured rays were a hidden and constitutive property of white light.
3. The part/whole distinction for the mass mereology discussed by Needham (2005) also requires the concept of 'affordance'. The parts of the sea extracted by buckets have the values of certain properties, such as quantity, determined by choice of bucket. The sea affords buckets full as well as thimbles full. However, it seems that there is no temptation to fall into a version of the second mereological fallacy in these examples. It is not a fallacy to declare that a bucket of water is a part of the sea.

Science progresses by asking whether there is a hidden property of the being which yields the affordance. When subject to the appropriate manipulations material substances afford spectra. But spectral colours are not parts of the substance that

affords them. Nevertheless, the question as to what distinguishes those constituent structures under which a substance affords an atomic spectrum of such and such a pattern and a substance which affords a different atomic spectrum is a legitimate question, the question of the grounding of affordances. According to Bohr's theory spectral affordances are grounded in configurations of electrons considered to be constituents of atoms. When we discover that incandescent sodium affords two yellow spectrum lines by passing the emitted light through a spectrometer what is affording this phenomenon – sodium atoms having a certain electronic configuration. If this makes sense, how have we managed to outflank the second mereological fallacy? We know there are no colours as constituents of atoms. In the Bohr conception of an atom it is taken for granted that electrons are *constituent*s of atoms because atoms afford electron phenomena under certain manipulations. Electrons are nothing like spectral colours, so it seems unproblematic to assign them to the category of constituents of the inner structures of atoms?

Molecular and atomic spectra play an important part in Mulliken's view of the nature of chemical beings (Mulliken 1932).[2] How do we set up an experiment to produce molecular affordances? Why is it illegitimate to project electron affordances back as constituents of atoms, but legitimate to project atom affordances back as constituents of molecules? The short answer is simply that there are clear criteria of identity, both numerical and qualitative, that serve to pick out atoms as material individuals. The metaphysical question was settled empirically by the development of the technique of the travelling tunnelling microscope for which Binnig and Rohrer (1986) were awarded the Nobel Prize. The shape and boundary of an individual atom could be traced out. Is there a corresponding procedure that would establish electrons as bounded individuals?

Mulliken's invention of the concept of 'molecular orbital' allowed him to maintain the Boylian style principle that 'atoms are constituents of molecules' as a basic mereological principle while steering clear of committing the second mereological fallacy of projecting electron-affordances back into molecules as constituents. If they are not constituents of atoms they cannot be constituents of molecules. Hence the move from interpreting the quantum mechanical formulation of the processes of chemical bonding as referring to 'orbitals' rather than 'orbits' (Llored and Harré 2011). As we will see this move also changes the kind of *model* with which molecular chemistry is made intelligible.

[2] I am grateful to J.-P. Llored for bringing Mulliken's way of using the quantum mechanics of electrons in explaining bonding without requiring the assumption of actual orbits.

8.6 Chemical Affordances

It is only too easy to carry the concept of an affordance further from dispositions and capacities to constituents. But as Earley (2005) argues the sea does not contain salt as a constituent– though it does contain sodium and chloride ions. As a result of subjecting sea water to a certain procedure, for example evaporation, it will afford that white crystalline substance we call 'salt' of which there is *none in the sea*. In light of the above discussion of mereology, Earley's insight can be expressed as pointing out an example of the second mereological fallacy. A frozen lake has the same molecular structure in case it affords walking to a wolf but does not afford walking to the moose it is stalking. The same structure explains its strength relative to the weight of a wolf and its weakness relative to the weight of a moose. Though an affordance is grounded in some feature of the substance from which it is elicited it is relative to the local situation. However, such a feature may have been proposed on the basis of shaky reasoning – in short from a move which involves the commission of the second mereological fallacy – going from products (affordances) to constituents, the grounding of affordances.

We do not have clear and determinate criteria for either the qualitative or the numerical identity of electrons. In so far as these 'items' are affordances on the lower edge of the chemical domain to build a realist theory of atomic structure on the basis of projecting them back as constituents of the atoms which afforded them is a mereological fallacy of the second type. J-P. Llored and I have written extensively about this fallacy in the context of Mulliken's introduction of molecular orbitals vice molecular orbits (Llored and Harré 2011). Orbits would be the *tracks* particulate electrons follow around molecules as binding the atomic constituents into a whole, but the conclusion from the existence of a certain kind of track to the existence of an electron or any other appropriate charged *particle* as an entity in all circumstances is fallacious (Harré 1990). So we come at this from two different directions. Tracks as observed in colliders are used to infer the existence of particles with certain properties, while the Mulliken move is to resist the reading back of electron affordances into orbiting bits of electrically charged stuff. Only by bringing in the concept of affordance and the second mereological fallacy are we able to sustain his intuition with a metaphysical argument.

However, there are clear and determinate criteria for the qualitative and numerical identity of atom-cores (ions) as affordances of certain procedures exercised on molecules, such as electrolysis, backed up by direct observation as described above in the use of travelling tunneling microscopes as developed by Gerd Binnig and Heinrich Rohrer (1986). To declare that molecules are structures of which the constituents are atomic cores is not a philosophical error.

To sum up the argument: we find a ubiquitous role played by electrons in chemical theory. Electrons-as-particles phenomena can be obtained from atoms by means of certain procedures such as the cloud chamber. Electrons as wave phenomena can be obtained from atoms by distinctive and independent procedures such as double slit experiments. But it does not follow that the electrons obtained

as particulate phenomena were parts of the atoms from which they were sourced. The principle behind this strong claim is something like this: it is at least a necessary condition for the products of an analysis to be ascribable to the whole from which they came as its parts that they share the same general criteria of individuation and identity. The dual nature of electrons as having particulate and undulatory attributes, at least at the level of chemical explanations, distinguishes them from atoms and from molecules. Is Bohr's inference to the planetary electron conception of the atom not just a superceded image of the nature of atoms, but also a mereological fallacy? More radically still, inspired by Mulliken's interpretation of quantum chemistry, should we not go further down this line and query the claim that molecules are *actually* structures of atom-cores? But that radical step is blocked by the work of Binnig and Rohrer.

To say that such and such an atom has this number of electrons in that shell and to use that hypothesis to account for some of its chemical properties, does not entail that there is a cloud of little charged particles orbiting the nucleus. But what is its status? According to the line of reasoning developed in this paper it can be no more than a mereological *model* of this kind of atom. It can hardly be disputed that knowledge of the physics of the subatomic level of reality plays an important part in the practice of chemistry. It is therefore not surprising that philosophical issues in the physics of that domain should also play a part in the philosophy of chemistry. What makes us think in terms of entities when we draw inferences about the electron yielding properties of atoms? Experiments can be devised to display the presence of electrons as tracks in cloud chambers, photographic emulsions and computer simulations (Harré 1990).

There are no orbits because there are no particulate electrons absent such devices as cloud chambers, but in what sense are there Mulliken orbitals? The way that Mulliken's proposal resolves the tensions in building a basic theory of chemical bonding on the second mereological fallacy can be seen in analyzing his insight in the light of the various procedures of model making and the different kind of models that ensue.

8.6.1 Models in Science

There are two kinds of models in use in the sciences (Harré 2006). They are differentiated by the relation of the model to that which it serves to model. A model has a *subject* – that which it is a model *of*, and it has a *source* – that which is it modeled *on*.

For some models the subject is also the source of the content of the model. These are the analytical models which are usually used to display the structure of some complex entity and are derived from that entity by abstracting relevant features. There may a several different analytical models of the same entity, for example the many geological models of the earth each created by abstracting only certain features, say geological strata as compared with the core and the mantle.

These are problem relative – there is a model for the blood system of a mammal and another for the nervous system, both abstracted from the body of the animal in question. To create an analytical model the anatomist must be able to observe the body of the animal in question as a concrete source of the abstract lay out of the various anatomical systems that can be represented in diagrams. Newton's model of the solar system as a system of perfect material spheres obeying Kepler's laws of motion and the inverse square law of gravitational attraction was derived by abstraction and idealization of observable fears of the actual solar system (Frigg 2010: 251–268). Analytical models can be wholly pictorial as in anatomy or they can be abstract and partially mathematical as in the Newtonian cosmology.

2. Some models are representations of subjects that are different from the sources of the content of the model – paramorphic models. Usually these models are created to fill gaps in our knowledge, particularly of the fine structure of substances under study. Watson and Crick made a model of something they had not observed, namely the previously unknown structure of the germ plasm. By attending to how the model behaved or could behave they found a sufficient number of analogues to the behavior of real DNA that the model quickly became authenticated as the structure of DNA. But best of all eventually experimental studies of the DNA molecule revealed a structure that was sufficiently similar to their model. Some paramorphic models such as the kinetic theory of gases quickly attract a mathematical as well as a pictorial interpretation.

The possibility of creating mathematical representations of analytical and paramorphic models leads to a second general distinction in model kinds.

Formal models are mathematical systems representing processes in such a way that representing the phenomena to be explained in mathematical terms, assigning values to variables, and then performing the requisite formal operations as representing whatever process is under study, yields new and consequential values for the relevant variables. Formal modeling is valuable for many scientific projects but unless supplemented by a material interpretation is empty as a source of explanations.

Iconic models are concrete representations of things and processes as they are or as they might be imagined to be in nature. Experimental programs can often be devised to explore the relevant natural domain to try to find such beings or good analogues of them. An iconic *model* exists in the same category as its subject – e.g. as a material thing, as a process, as an abstract structure. A model is related to its subject by similarities and differences – in general a model is an analogue of its subject (and a subject is an analogue of any of its models). Model based cognition depends on semantics (content) of a discourse rather than its syntax (logical form). Iconic models play an important role in providing explanations of phenomena. For example, they can be used as representations of the so far unobserved generative mechanisms that underlie observed processes, and are used to support hypotheses as to the causes of phenomena. For the most part they represent the internal features of the entities in which causal patterns are observed and affordances obtained. For example Bohr's planetary electron shell model of the internal constitution of atoms explained the spectra obtained from many chemical elements.

The representational content of iconic models makes possible the testing of the model not only for empirical adequacy, (does it enable successful predictions and retrodictions of phenomena to be made?) but for ontological plausibility. Is there something similar in the real world which not only behaves as the model is imagined to behave but also is of the same general nature? Is there a molecular double helix in the germ plasm sufficiently similar to that presented as a representation in the Watson-Crick model? Of course, 'sufficiently similar' is a criterion that comes in degrees and changes with the technology available. The work of Binnig and Rohrer, cited above, is a nice example of the empirical establishment of the authenticity of a model as a representation of something in the material world by picking out individual atoms.

Given the above insights what can we say about the role of entitative concepts of electrons in chemical understandings of atoms? The core of G. N. Lewis's bonding theory (1926) involves just such a conception of electrons as does the early Bohr planetary model of the atom. And there lies the clue – it is not a mereological fallacy to build a planetary *model* of the composition of atoms for heuristic purposes of chemistry. How are we to assess the plausibility of models of the internal constitution of atoms in relation to the role of this concept in chemistry? Provided we use the model as a source of ideas about a mathematical representation of the processes being modeled and resist material claims we are on sound ground.

Since we are not able to study the internal constitution of atoms by the kind of methods we might use to study the internal constitution of a tape worm by dissection and abstraction from what we observe, models of atomic 'innards' cannot be analytical in the above sense. Nor can they be iconic, since to project only one of the properties of product electrons back in to the structure of an atom is to commit the second mereological fallacy. Clearly, the planetary electron hypothesis, if taken seriously as a contribution to our knowledge of the internal constitution of atoms, is an example of that fallacy. The only remaining possibility is Mulliken's inspired proposal that we clearly disassociate ourselves from 'electrons and their orbits' by proposing a pregnant new concept – that of the 'orbital'. It reminds us of the history of quantum chemistry from its beginnings in Bohrian 'orbits', but offers a purely formal model of the structure of chemical entities.

Mulliken's move from thinking in terms of orbits, an iconic model, to thinking in terms of orbitals, a mathematical model, has the effect of retaining the electromagnetic model of the atom, with all the apparatus of spin etc., as a valuable aid to thinking about problems in chemistry at this level, but only heuristically. There can be no inference as to that is how atoms are. That would be to commit the second mereological fallacy.

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Chapter 9
Metaphor in Chemistry: An Examination of Chemical Metaphor

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The history of definitions of metaphor is a history of hopeful efforts, none of which fully succeed in providing a satisfying answer to the question of what it is. Aristotle's original attempts to grapple with metaphor continue to inform (or infect) contemporary definitions of the term. "Metaphor consists in giving the thing a name that belongs to something else" [Aristotle *Poetics* 1457b5] on the basis of some kind of similarity. Everyone uses metaphor to communicate, but when aptly made, a metaphor is "strange" yet "sweet," and thus "most brings about the learning" . . . but shaping good metaphors requires a special kind of genius that "cannot be learned from anyone else" [Aristotle *Rhetoric* 1410b]. Metaphor is a strange mix of the familiar and the unfamiliar, it is common and a mark of genius. For Aristotle a metaphor may connect two familiar things in unfamiliar ways such that the strangeness of it may be instructive. More commonly, metaphor is defined as that which associates an unfamiliar term with a familiar one in order to illuminate the former in light of its similarity with the latter. Aristotle's first definition seems banally simple: metaphor makes one thing stand for another.

The vagueness and generality of these definitions suggests an ineradicable circularity from the start: definitions of metaphor inevitably rely on metaphors. For example, the very notion of "standing" for something is itself a metaphor, one that has great significance in jurisprudence. The notions of familiarity, similarity, and their cognates, which lie at the heart of so many definitions of metaphor, are themselves metaphorical concepts. Metaphor is an oddly self-referential bit of language whose description can only ever be a performance of its meaning.

The following seven sections begin with a discussion of metaphor in science generally, then proceed to an examination of its role in chemical thinking in three

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contexts: the history and philosophy of chemistry, laboratory research practice, and chemical education. The chapter concludes with a section on the specifically chemical understanding of metaphor.

9.1 Metaphor in Science

The positive role of metaphor in science has been noted by philosophers, historians of chemistry,[1] science education researchers and educators[2] where it has often been hailed as a descriptive and explanatory device that stimulates and shapes concept development. Several philosophers[3] have noted the ubiquity of metaphor and proposed that *all* language is metaphorical. In his masterful treatment of that act of metaphoring, philosopher Kuang-Ming Wu, presents an extensive cross-cultural hermeneutical survey of the variety of attempts to define metaphor. He finds all of them incomplete, though each one may be more or less helpful regarding some aspect. Not so helpful are attempts to treat metaphor as one among several figures of speech, and subsequent attempts to split hairs among them. I follow Wu in his treatment of simile, metonymy and other non-literal forms, as different kinds of metaphoric activity, for in order to achieve the effects for which they are so often called upon, *all non-literal forms of language rely on metaphoring*. It is most beneficial, therefore, to see metaphor as a general form of communication activity, rather than as a specific linguistic formula that follows specific rules.[4] Any attempt at hardening a definition of metaphor inevitably cracks up as novel forms of expression and understanding naturally emerge from cultural advancement.

Before moving on to discuss the specific case of metaphor in science, we may bring these general considerations of metaphor and language full circle in the context of Alfred North Whitehead's "fallacy of the perfect dictionary." Like other fallacies Whitehead introduces in the course of his philosophical reflections on science, this one points to the seemingly natural tendency of thought to capture the dynamism of concrete reality in static abstractions. One who commits the fallacy of the perfect dictionary misconceives both language and thought:

> There is an insistent presupposition continually sterilizing philosophic thought. It is the belief, the very natural belief, that mankind has consciously entertained all the fundamental ideas which are applicable to its experience. Further it is held that human language, in single words or in phrases, explicitly expresses these ideas. I will term this presupposition, "The Fallacy of the Perfect Dictionary." (Whitehead 1938, 173)

[1] T. Nummedal (2011), Bensaude-Vincent and Stengers (1996), Newman and Principe (1998), Dobbs (2002), Merchant (1980), and others.

[2] Jeppsson et al. (2013), Aubusson et al. (2006), Tobin and Tippins (1996), Hofmann (1990) and others.

[3] Black (1962), Cassirer (1953), Hesse (1966, 1988), Harré and Martin (1982), among others.

[4] This is, in fact, what Cassirer (1953) called "radical metaphor" and Kuhn (1977; 1979) referred to as "metaphor-like processes." This theme is discussed in depth in Sects. 9.5 and 9.6 below.

Whitehead uses the fallacy to distinguish two philosophical attitudes: the "critical school" and the "speculative school:"

> The critical school confines itself to verbal analysis within the limits of the dictionary. The speculative school appeals to direct insight, and endeavors to indicate its meanings by further appeal to situations which promote such specific insights. It then enlarges the dictionary. (Whitehead 1938, 173)

Cultures advance, languages continually change, as does thought. In the midst of all of this change, the speculative school of philosophy finds in metaphor an engine of change, the source of linguistic and conceptual growth. In addition to those mentioned earlier, Bailer-Jones (2000, 2002), Ricouer (1981) and Miller (1996) are among philosophers who subscribe to the creative potential of metaphor in the science.

Metaphor, as Aristotle indicated, helps to make the unfamiliar familiar, but the current of meaning can flow both ways: the familiar can also be rendered unfamiliar enough to appear novel, strange and interesting. The dialectic of novelty and confirmation, so important to the Shannon definition of information, is also at play in the way that metaphor functions. How much a metaphor would lean towards confirmation or novelty, its signal-to-noise ratio in a given context, depends on a variety of complex factors. In this paper, we limit the contexts to those of education and research. Considered abstractly, education and research are polar opposites: research seeks novelty in the form of invention and discovery, while education strives to confirm the next generation of researchers by assuring their mastery of basic vocabularies, concepts and skills. But we must avoid mistaking these abstractions for concrete actualities.[5] While education generally leans more toward confirmation-oriented uses of metaphor, opportunities for student research may sometimes lead to breakthroughs. And whereas research is often geared toward the creation of novel metaphors in the process of model building, there are perhaps too many cases of research that merely confirm and solidify the hold of a given approach. The creative potential of science is enhanced whenever metacognition is engaged in education or research, that is, when the function of metaphor in scientific thinking is acknowledged and, to whatever extent, understood and applied.[6]

Like Niels Bohr's horseshoe,[7] metaphor works whether or not one recognizes it *as* metaphor. And once it gains sufficient currency it is no longer considered metaphorical: it has made the transition from non-literal to literal. Commitment to a metaphor's literal "truth" has to last only as long as its ability to move inquiry

[5] The National Science Foundation and other science agencies have sought to dispel institutional tendencies to polarize the two modes of practice by issuing funding solicitations that call for integrative undergraduate science curricula. For example the NSF's Undergraduate Research Centers.

[6] See Graves' (2005) treatment of this theme in Sect. 9.4, and Bhushan and Rosenfeld's (1995) treatment in Sect. 9.5, below.

[7] As the story goes, a visiting physicist commented on a horseshoe hanging above the doorway of Bohr's country home, "Bohr, I didn't know you believed in such superstitions!" to which Bohr responded: "I don't, but I've heard that it works whether or not one believes in it."

forward; literal truth has no permanent status as literal and its lifespan is not known in advance of its employment. The creative power of metaphor is its *liminality*; this is also the source of its disruptive power. Paul Ricouer has noted that metaphor, like poetry, plays on the boundary between dogmatic commitment and speculative distance:

> What is given to thought in this way by the 'tensional' truth of poetry is the primordial, most hidden dialectic – the dialectic that reigns between the experience of belonging as a whole and the power of distantiation that opens up the space of speculative thought. (1981, 371)

Metaphor enables the participation mystique of true dogma while maintaining a potential distance from the matter at hand (e.g., from the theoretical framework or model used in a given research project), thus providing a cognitive wedge that opens a space for speculation.

Awareness of metaphor *as metaphor* renders its semantic frame *labile*—an important feature during times of conceptual fluctuation and growth… which come at an increasingly rapid pace for new areas of research. For Rom Harré the necessity of resorting to metaphor can be stated very simply:

> We need metaphor because in some cases it is the only way to say what we mean since the existing semantic fields of current terminology referentially related to the subject in question are inadequate to our own thought. (Harré and Martin 1982, 95)

He considers metaphor to be an interventional tool rather than representational one.[8] Metaphor's capacity to make a difference for a given inquiry is what matters, not its ability to accurately represent phenomena in various circumstances. The pragmatic aspect of metaphor puts its semantic lability to work to facilitate inquiry. Therefore, epistemological commitment to metaphor is justifiably flexible. A metaphor that is successfully put to use for a specific purpose may lose its usefulness, only to find it again if a new problem activates its multivalent potentials.

9.2 The Metaphor at the Foundations of Chemistry: Defining Element

A self-reflexive commitment to metaphor remains aware of its opportunities and limits, even when these have yet to be discovered with precision. This way of holding metaphor in mind makes particular sense in the context of chemistry. A significant case is found in the official International Union of Pure and Applied Chemistry (IUPAC) definition of chemical element, which, in an unusual turn, embodies a key duality.[9] On the one hand element is defined as *atom*, on the other hand as *substance*:

[8] As does Ian Hacking's (1983) *Representing and Intervening*.

[9] A full discussion of the development of this definition and its impact on chemical research and education appears Sect. 9.6 of this chapter.

1. *A species of atoms*; all atoms with the same number of protons in the atomic nucleus.
2. *A pure chemical substance* composed of atoms with the same number of protons in the atomic nucleus. Sometimes this concept is called the elementary substance as distinct from the chemical element as defined under 1, but mostly the term chemical element is used for both concepts. [http://goldbook.iupac.org/C01022.html]

The relation between the two sub-definitions is similar to that which metaphor posits between any pair of subjects. No matter how subtle or great the difference between them, pairings of this kind open a space, as Ricouer noted, for speculation. A careful pairing of similarities and differences is, after all, the business of metaphor. An analogy can be drawn between metaphoric pairings and the pairing of wine and food: the pairing brings out latent flavors in both. In gustatory pairings, flavors are amplified or diminished by combination. A metaphoric pairing is more complex in that it operates in the polysemic medium of language.

Ordinary language is by nature polysemic: individual words, not to mention phrases and statements, may admit of more than one meaning. Polysemic potential is further broadened by taking pragmatic and contextual considerations into account. Polysemy is an aspect of every language but scientific language strives to eliminate conceptual ambiguity by reducing the polysemic potential of key terms. Examples of this are to be found in chemical nomenclature and the formal definition of terms by professional societies, such as IUPAC.

In light of this fact, finding explicit bivalence in the official definition of 'chemical element,' at the very heart of chemistry, seems odd. The historical and disciplinary reasons behind it have been the topic of several articles in the philosophy of chemistry arena.[10] The definition originated with Fritz Paneth in 1931, in association with his successful work on the status of isotopes, which had been a vexing problem of early twentieth century chemistry.

Paneth explicitly accounted for his bivalent definition employing the metaphor of "oscillation" (*Schwanken*) to explicitly note its function in chemical thinking. He introduced this metaphor in the historical context of the Boyle-Spinoza debate over nitre:

> Boyle's statement that nitre 'consists' of volatile nitric acid and a solid residue shows just that *oscillation* [*Schwanken*] *between the naive-realistic and the transcendental meanings of the terms* which we exhibited above as particularly characteristic of the concept of element. (Paneth 2003, 136, emphasis original)

This historical illustration comes at the end of Paneth's two-part article (originally published in 1931[11]) whose purpose was to illustrate the epistemology of specifically chemical thinking. Though he does not label it as a metaphor, he takes advantage of the metaphoric potential of this dual-mode definition of chemical element. The self-reflexive use of metaphor in chemistry potentiates one's

[10] See, among others, Earley (2009), Harré (2010), Mahootian (2013), Ruthenberg (2009), and Scerri (2000, 2005, 2009), and of course Paneth (1931/1962), who originated this definition.

[11] It was translated into English for publication in 1962 as "The epistemological status of the chemical concept of element" in *British Journal of the Philosophy of Science*. 13, 1–14 and 144–160; it was reprinted in *Foundations of Chemistry 5*, 2003, 113–145.

awareness of various frameworks of explanation, including disciplinary, conceptual, instrumental, etc. Paneth explicitly noted two frameworks— naïve realism and transcendental idealism—as the ones operative in the case of chemical element. I generalize Paneth's point in my (admittedly metaphorical) re-description of metaphor as that which enables and directs deliberate transitions between explanatory frames as needs arise in practical contexts of research, teaching, or engineering. Naïve realism and transcendental idealism are only two possibilities among many (Mahootian 2013). I claim that while such transitions are apparent in the history of any empirically grounded discipline, chemistry contains some of the clearest illustrations.

9.3 Metaphor in the History of Chemistry

With the growing general interest in metaphor there has been corresponding increase in the literature on metaphor in the philosophy of science. An excellent survey of the topic, by Daniela Bailer-Jones, appears in the *Blackwell Guide to the Philosophy of Science*. The closing line of her chapter provides a segue for discussing the history of chemistry, as it highlights the inextricable links between model, metaphor, practice and ordinary language. She notes that

> beyond the commonalties of scientific models and metaphor already highlighted, there is one other: scientific models appear to be, contrary to past research traditions, as central in scientific practice for describing and communicating aspects of the empirical world as metaphors are in ordinary language. (Bailer-Jones 2002, 127)

Bailer-Jones speculates analogically about this pair of pairs:

> model: scientific practice : : metaphor : ordinary language

The analogy is not simple, as there are multiple interrelations between the four terms. Her main intent seems to be to illuminate the role of models in scientific practice as being similar to that of metaphor in ordinary language. However, because of the ambiguous role of ordinary language in scientific practice, and especially because of the function of metaphor in modeling (and of models in metaphoring), the analogy can readily be made to work in several directions at once, making the nexus of relations among the four more metaphorical than a straightforward (e.g. scientific) analogy should allow. Aristotle proposed that within metaphor the familiar term illuminates the unfamiliar, but one may as well assert that familiar and unfamiliar illuminate one another, occasionally trading places with sometimes surprising results.[12] Such surprises often occur when

[12] Analytic philosopher, Max Black (1962) applied rhetoric theoretician I.A. Richards' interaction theory of metaphor in this manner. Kuang-Ming Wu's (2001) cross-cultural hermeneutic approach to metaphor affirms this point with examples from several contexts and languages.

familiar terms, models, instruments, etc., are applied to objects and domains beyond those in and for which they were originally designed and intended.

Mary Jo Nye's conceptual history of chemistry, *From Chemical Philosophy to Theoretical Chemistry*, self-consciously traces the development of a specifically chemical approach to science, as distinct from physics. Nye briefly notes the relevance of metaphor throughout the history of chemistry and discusses specific examples in the eighteenth and nineteenth centuries.[13] She distinguishes "conventionalized metaphor," what nineteenth century chemist Wurz referred to as "a way of expressing a fact rather than giving an explanation," from whimsical and playful descriptions, such as A. Laurent's 1854 descriptions of atoms on the "chase," in "copulation," and in "marriages of convenience" (Nye 1994, 78–80). But all metaphor is a play on language and an alteration of everyday usage. While the extremes seem obviously distinct, the line that divides them is not easily discerned—certainly not during the period when such metaphors are suggested. For "as the problems change, so, often, does the standard that distinguishes a real scientific solution from a mere metaphysical speculation, word game, or mathematical play." (Kuhn 1962, 103)

The history of the concept of chemical affinity presents an interesting case in point. Nye demonstrates how this concept, originally considered explanatory, was later rejected in the light of other concepts and relevant new experimental data. The affinity concept reaches from its ancient origins in alchemy (like attracts like[14]), to its application in E. F. Geoffroy's 1718 table of chemical "*rapports*" for replacement reactions. The concept enjoyed new acceptance with H. Boerhaave's (1733) subsequent reinterpretation of affinity in terms of Newtonian forces of attraction and repulsion. Chemical affinity's gradual decline from mid- to late-nineteenth century, culminated in its rejection by J. L. Meyer as merely fictional. Nevertheless, the concept played an important role in the development of thermodynamic models of chemical reaction, and in the classifications of chemical elements. Nye's foreclosure on the nineteenth century history of affinity is somewhat premature, Meyer's objections notwithstanding. The concept enjoyed active use into the twentieth century: Van't Hoff refers positively to affinity as a central link in his 1907 Nobel prize winning integration of gas laws and osmotic pressure.

[13] Nye completely excludes alchemy from her account—this is an important omission that follows in the steps of nineteenth and early twentieth century historiography of science. I. Stengers and B. Bensaude-Vincent's *History of Chemistry*, published only a few years after Nye (1994), showed how fundamental concepts of chemistry, such as analysis, isolation and purification were developed to a high degree of sophistication. From the late 1990s to the early 2000s, W. Newman and L. Principe provided a wealth of documentary evidence to support the inclusion of alchemy in the history of chemistry. Tara Nummedal discusses the versatility of alchemy's promotion of chemistry.

[14] The term "like attracts like" still enjoys broad usage ranging from matchmaking websites to titles and abstracts of research articles in academic journals of physics, chemistry and molecular biology.

Stepping back from details such as this, Nye's narrative of the positive role metaphor plays in chemistry is generally on target:

> The role of metaphor in defining a scientific object and suggesting a method of investigation is demonstrated in the history of the chemical discipline, both in the development of conventional *definitions* of the causes of chemical effects and in the working out of a *system*, which, by describing substances in the language of natural history, encouraged chemists to think about these objects along genealogical and morphological lines. (Nye 1994, 78; italics original)

The gain of epistemic access through metaphor is gradual. It occurs as a dialectical process that begins with epistemic commitment to a conceptual metaphor, which inevitably means commitment to some level of conceptual error. In the course of applying the metaphor in model-building (e.g. Harré and Martin 1982), we observe an alternating series of reifications and retreats from reification. In the centuries-long transition from chemical affinities to thermodynamics, we can trace the career of the mythical idea of nature as organism, to the metaphorical idea of "like attracts like" (which shaped sympathetic magic and alchemical thinking in pre-modern Europe), to eighteenth century affinity tables, and finally to the gradual refinement of the idea of energy and energetic relationships among chemical compounds in various reaction environments. Such adjustments are made in the context of chemical practice: the more or less coordinated but always interdependent and mutual refinement of concepts, instruments, experimental design and observational targets. In this respect, contemporary studies of "science in practice" bear similarities with science education studies.

9.4 Metaphor in a Solid State Physics Lab

In this section, we focus on the uses of metaphor in a contemporary research lab. Heather Graves spent 7 months studying the rhetoric of inquiry in a solid state physics lab with a seasoned researcher and his graduate students. She focused much of her time on research about amorphous semiconductors, specifically, persistent photoconductivity. What Graves learned about the function of metaphor in this context can be readily transferred to our study of chemistry.

Rhetoric In(*to*) *Science*: *Style as Invention in Inquiry* (Graves 2005), argues that since the time of Robert Boyle, and culminating in the work of Joseph Priestly, science has appropriated the rhetoric of invention theory into scientific method. One of the founders of experimental method, Boyle considered it important to communicate what and how he thought about his experiments, taking pains to recreate his thinking in the mind of his reader (recall Whitehead's characterization of speculative philosophers, in Sect. 9.1, above). He made this an explicit goal of his style of writing. Both he and Priestly held metaphor and analogy to be far more than merely decorative or persuasive: both saw metaphor as a means of "meditating" and "reflecting" upon ideas. Both considered metaphor as a chief means of associating and extending ideas by "transferring similarities" from one domain to another. This transference is explicitly discussed by Priestly in both his scientific and religious writings (Graves 2005, 75).

Graves reports that her interactions with lab director Edward MacDonald (a pseudonym) stimulated him to do his science "aloud." This provided her with several opportunities to record the development of analogies and metaphors. She noted varying degrees of success in the application of metaphors and analogies to the task of interpreting experimental data. Normally, MacDonald would sit at the computer, revising and deleting, until he had the most unambiguous text for the purpose of communicating research findings. Graves' in-depth analysis of several episodes of experimental work by MacDonald and his research team, demonstrates the epistemic contribution of rhetoric in a number of instances. Most of her observations pertain to the re-interpretation of experimental findings in the course of preparing an article draft for publication. She shows how such discussions were often coupled with refinements to the lab's research strategy.

To conclude this section I note that Graves' discussion of the use of analogy, metaphor and metonymy[15] in the research process is consistent with previous work in this area; while there are several instances to draw upon, only two will be noted. The first instance confirms Mary Hesse's (1980) understanding of the function of analogy in science research: MacDonald first predicts and later confirms a particular phenomenon. The analogy he draws between hoodoos and an amorphous silicon nitride superlattice cross-section, "establishes three known terms with the purpose of predicting a fourth unknown term" (Graves 2005, 102).

In contrast with those who focus on the discursive qualities of science but not its practice, and those who focus on its practice but not on its rhetoric, Graves focuses on the role of rhetoric in the process of inquiry (Graves 2005, 2). In so doing, she clarifies one aspect of the role of metaphor in concept formation in and through the process of grappling with data and models. The key link in this process is the act of *invention* wherein novelty is introduced to the practice of science by "mangling" data, theory and interpretation. The "mangle of practice,"[16] as Andrew Pickering calls it characterizes the concrete practice of lab bench science. As a quantum physicist, Pickering's (1984) research experience with quarks led him to reflect on the practice of science and the articulation of the mangle. He summarizes the process:

> modeling has an important real-time structure, with contours of cultural extension being determined by the emergence of resistances, and by the success or failure of 'accommodations' to resistance... This temporal structuring of practice as a dialectic of resistance and accommodation is, in the first instance, what I have come to call the mangle of practice. (Pickering 1995, xi)

[15] Graves focuses more of her analysis on the lab's use of metonyms than on metaphors, however, the case has been made in section 1 above, that the various genera of non-literal usages of language actually *function metaphorically*, even if they are not identical in form to metaphors. Kuhn's (1977, 1979) and Cassirer's (1953) discussions of this idea are found in Sects. 9.5 and 9.6, below.

[16] Pickering's seemingly odd choice of this term harks back to old-time clothes washing machines which had no spin cycle. Instead, wet clothing were put through the ringer and the resulting "mangle" consisted of diverse items of damp clothing pressed into a single, flat, apparently continuous plank.

At various points in the research cycle, as researchers inevitably encounter results that are somewhat different than expected, they will alter the *ceteris paribus* conditions, the explanatory model, the selection of relevant theories, the boundary conditions of the phenomena under scrutiny, even the standard operating procedures of their laboratory equipment. Essentially anything, whether theoretical or instrumental, that can be bent to its near-breaking point will be bent; theory and model will be made to accommodate instruments and experiment design and vice versa, until expectations of acceptable experimental outcomes closely match actual experimental outcomes.

Graves' analysis of the rhetoric of invention in MacDonald's descriptions of his research team's model-building efforts is consistent with Pickering's understanding of the mangle of practice. MacDonald and his co-workers undertook to modify standard solid state physics models in order to fit the diverse experimental settings for which they were not originally designed; in some cases, modifications were stimulated by peer-review comments accompanying the rejection of their article for publication in a journal.

9.5 Metaphor in Chemistry Education

Nalini Bhushan and Stuart Rosenfeld's 1995 article, "Metaphorical Models in Chemistry," offers an analysis of metaphor in reference to scientific modeling in the service of pedagogy in chemical education. The authors cite James Hofmann's (1990) study of "How the Models of Chemistry Vie," a play on Nancy Cartwright's (1983) *How the Laws of Physics Lie*. Hoffmann distinguishes two functions of models in chemistry as "the culmination of phenomenology and the commencement of explanation" (Hofmann 1990, 406). The former offers "specific causal scenarios," while the latter presents "unifying explanatory formalisms." Oddly, Bhushan and Rosenfeld substitute these functions with the not exactly equivalent pairing of "predictive" vs. "insightful." The derivation of causal scenarios from predictive ones, and explanatory formalisms from insightful ones requires clarification. In the context of their discussion, Bhushan and Rosenfeld note that "[a] working view for students might be that models should be seen as tools for prediction and correlation but that one should remain aware of their metaphorical standing." (Bhushan and Rosenfeld 1995, 579). An understanding of the "standing" of models as metaphorical is sufficient to arm the student against swallowing the model whole, as it were, and taking it as literal truth. Bhushan and Rosenfeld consider this to be good pedagogy. Furthermore, they note that *both* aspects, prediction and insight, are metaphorical, since it is "not so odd to view computational models as metaphorical" [581].

Though they don't say so explicitly, their pedagogy elucidates the metaphorical nature of models in order to disabuse students from habitually thinking of models as representations. Bhushan and Rosenfeld's pedagogical ideals seem consistent with thinking about models as interventions rather than literal descriptions.

Although the authors conclude their article with the following passage, it is unclear whether, in the final sentence, they are using the term model in a metaphorical way:

> Our own lack of attention to the metaphorical nature of a particular model can blind us as teachers to certain misunderstandings of students. As we use models in teaching, it may be important to recognize that the leading edge, and perhaps *the most important part of the model for students*, *is the metaphor*. Indeed, we might say that where we use models in our teaching, the metaphor is the currency of the teacher-student transaction. [582]

Indeed, they introduce a metaphor, i.e., the *currency* of a transaction, to characterize their own use of metaphor. This would seem to reinforce Bailer-Jones' closing statement which exhorts us to consider whether model may be as ubiquitous in science as metaphor is acknowledged to be in language. Furthermore, Bhushan and Rosenfeld's currency metaphor makes explicit a value orientation that Mary Hesse asserted as a necessary part of metaphor. In Hesse's words, is an "evaluative interpretation," i.e., one that takes a "proper stance" toward the phenomenon in question and thus "implies that metaphor is concerned with action as well as description" (Hesse 1988, 14). This is also consistent with Thomas Kuhn's remarks on metaphor and science education.

In his later writings, Kuhn highlights the work of metaphor in the education of naïve science students as a case of changing "*seeing*" into "*seeing as*," for example, seeing certain spots in a microscope as microorganisms. Making invisibles *visible* also makes other visibles *invisible* in order to clear the way, so to speak, toward the newly identified target. Kuhn takes metaphor to be "essentially a higher-level of the process by which ostention enters into the establishment of reference for natural kind terms" (Kuhn 1979, 537). In "Second Thoughts on Paradigms," he deals with the related question, "How do scientists attach symbolic expressions to nature?" Kuhn couches his answer in terms of the activity of "recognizing similarity sets," or transforming seeing into *seeing-as*. To successfully solve the problems in a science textbook requires just this ability. "The student discovers a way to see his problem as like a problem he has already encountered. Once that likeness has been seen, only manipulative difficulties remain" (Kuhn 1977, 470) Science education, according to Kuhn, involves conveying to the student *a body of standard examples* ("exemplars" or paradigms). "Acquiring an arsenal of exemplars, just as much as learning symbolic generalizations, is integral to the process by which a student gains access to the cognitive achievements of his disciplinary group" (Kuhn 1977, 471). These exemplars are often in the form of specific problems and their solutions which have been raised from the myriad situations encountered in naive experience. There are several standard metaphors in these statements that might attract the usual kinds of attention (inquiry as a war that requires an "arsenal") but I would direct our attention to a deeper layer: attachment, as in the "attachment of symbolic expressions to nature" (Kuhn 1977, 467). The process of reference-fixing, or "dubbing," is what Kuhn calls a "metaphor-like process," which he considers more fundamental and less obvious than the similar process operative in metaphor. "Metaphor plays an essential role establishing links *between scientific language and the world*." (Kuhn 1979, 539, emphasis added).

The *establishment* of "similarity sets" is a specialty of the metaphoric mode of discourse. Kuhn notes that "[it] is sometimes (perhaps always) revealing to view metaphor as creating or calling forth the similarities upon which its function depends. With that position I very much agree"(Kuhn 1979, 533). The process of scientific education, as well as that of scientific discovery and invention, involves just this kind of mental transmutation: a creation of categories by means of elevating certain impressions from the realm of naïve realism into the realm of scientific significance. Kuhn approaches this conception, finally dropping the distinction between metaphor and metaphor-like processes, for the sake of brevity:

> 'metaphor' refers to all those processes in which the juxtaposition either of terms or of concrete examples calls forth a network of similarities which help to determine the way in which *language attaches to the world*. (Kuhn 1979, 539 emphasis added)

Whether or not Kuhn is aware of this (and there is no indication of this in his writing), the idea of any *attachment* of language to the world itself is metaphorical. Ernst Cassirer, on the other hand makes this an explicit claim that lies at the basis of his *Philosophy of Symbolic Forms*. For Cassirer, the very act of speech, the act of attaching thought to a medium that is fundamentally different from thought (i.e., sound) is itself an embodiment of metaphor, as one thing is made to stand for another. Cassirer also notes that "radical" metaphors don't merely point out similarities and dissimilarities, *they institute them*. This is one manner in which metaphorical commitment has practical, even material impact.

The question of how conceptual categories are first instituted is relevant to both research and education. A recent study of the use of metaphor in science by education researcher, Frederik Jeppsson and his co authors[17] makes three key claims about the role of conceptual metaphor (CM) in scientific problem solving. In the course of making these claims, the authors review much of the literature of education theory on this topic and affirm a key point that is of interest to my analysis: the question of whether experts and novices share conceptual strategies, or employ distinct ones in solving scientific problems. Until recently the latter position[18] was favored, but recent evidence arising from education research has provided support to the former position, represented in the work of Gupta et al. For example, according to Gupta, novice and expert use similar conceptual resources, but in addition to having a broader variety of CMs, experts have greater *flexibility* with regard to the ones they use. In their studies, Gupta et al. show that both expert and novice use basic CMs drawn from everyday experience, often reifying concepts or processes, for example, treating them as material substances in the course of reasoning about them. Whatever may be the degree to which experts use concrete metaphors instead of the "abstract" and "constraint-based"[19] ones specific to a given disciplinary discourse, they switch seamlessly between CMs.

[17] Fredrik Jeppsson et al. (2013) Exploring the Use of Conceptual Metaphors in Solving Problems on Entropy, *Journal of the Learning Sciences*, *22*:*1*, 70–120.

[18] See Jeppsson et al. (2013, 72).

[19] Jeppsson et al. (2013, 72).

The switch may occur between different phases of the research process, and/or between doing research and teaching. This finding confirms the liminality of metaphor discussed in Sect. 9.1, above.

Gupta found that besides reifying concepts as material substance, researchers also engaged in metaphorical identification with and projection of agency. These tendencies were exemplified in Graves' observation of MacDonald's researchers. These tendencies are consistent with the definition of metaphor as a rhetorical form that introduces something unfamiliar in terms of something familiar. There are other compelling reasons for favoring Jeppsson's presentation of the continuity between expert and novice. The history of science is full of stories about how the expert's mentality mingles with that of the novice in the initial framing of an incorrect model. Thompson's plum pudding model and Rutherford's solar system model of the atom were later refined by others in the course of trying to apply them in theory building and experimental design.

Ernst Cassirer's neo-Kantian epistemology grounds his *Philosophy of Symbolic Forms*[20] on the continuity between different modes of symbolic thinking, with mythic and scientific thinking occupying the extremes. Rather than summarize its argument here, I note that some of his key conclusions are supportive of the continuity thesis developed by Gupta et al., and incorporated in the claims of Jeppsson et al. The following excerpt from Cassirer's chapter on "The Power of Metaphor" suffices to show the consistency of his analysis with what Jeppsson et al. note as the crucial feature of expert knowledge: flexibility with respect to choices among conceptual metaphors, and a metacognitive grasp of such decision-making and implementation. Cassirer talks about the final stages in the development of thought, wherein self-consciousness is characterized by self-possession. At its final stages of development, thought is no longer compelled by concrete aspects of imagination that shape the two instruments that co-evolved, and thus co-determine one another, namely, language and myth.

> Word and mythic image, which once confronted the human mind as hard realistic powers, have now cast off all reality and effectuality; they have become a light, bright ether in which the spirit can move without let or hindrance. This liberation is achieved not because the mind throws aside the sensuous forms of word and image, but in that it uses them both as *organs* of its own, and thereby recognizes them for what they really are: forms of its own self-revelation. (Cassirer 1953, 99)

The idea of the scientific mind using word and image as "organs of its own. . .self-revelation" is especially important: in scientific problem solving experts *consciously* choose to use materialistic (and other concrete) metaphors drawn from daily life. That is, for as long as it is useful, the expert knowingly acts *as if* the metaphor is literal, then switches to a more abstract metaphor for which there is no experiential basis, or even runs contrary to the expectations of naïve experience.

[20] In three volumes (1925–1929) Yale University Press. Cassirer draws on a broad multidisciplinary pool of evidence from human, social and physical science of the mid-twentieth century.

On such occasions, the expert's recourse to seamlessly juxtaposing qualitative and quantitative thinking whenever possible (ala Jeppsson), enables powerful inferential moves facilitated by a range of mathematical formulae. The whole range of modes, from concrete metaphor to abstract mathematical relation, is used in various stages of scientific inquiry, whether the inquirer is novice or expert. The differences between them emerge with the sophistication of abstractions, on the one hand, and the facility of movement between abstraction and concreteness when need and opportunity arise.

9.6 A Chemical Concept of Metaphor: Reconsidering the Chemical Element

Let us return at last to the definition of chemical element, as established by IUPAC. I consider the most intriguing part of Paneth's formulation of this concept of element to be the necessity of *schwanken*, the oscillation[21] between the abstract transcendental and the concrete naïve realist view. In an earlier section of this chapter we noted that this definition suspends the concept of element in a space of speculation between the two poles in much the same way that metaphor suspends judgment between intersecting sets of alternative meanings. Where definitions are intended to attenuate the inherent polysemy of language, metaphor activates multiple sets. The unique feature of the IUPAC definition, seen below, is that it wants it both ways: the distinction is spelled out in the second definition but withdrawn by the end:

1. *A species of atoms*; all atoms with the same number of protons in the atomic nucleus.
2. *A pure chemical substance* composed of atoms with the same number of protons in the atomic nucleus. Sometimes this concept is called the elementary substance as distinct from the chemical element as defined under 1, but mostly the term chemical element is used for both concepts. [http://goldbook.iupac.org/C01022.html]

It is interesting that both definitions of chemical element are deemed necessary, that neither can be reduced to its partner, nor can both be reduced to a simpler definition. Two definitions of element are brought together as partner terms in a metaphor. There is an irreducible space between them and this is what metaphor posits between similars. The relation between them is not only semantic or syntactic, it is pragmatic: it does what Hesse refers to as taking a "stance" on the world. The relational space between the definitions draws on potential domains of application, potential relevance-determining contexts. The chemist's practice is shaped by existing theoretical models that *more or less* fit the experiment design,

[21] Mahootian 2013 "Paneth's epistemology of chemical elements in light of Kant's *Opus postumum*." *Foundations of Chemistry* 15:171–184.

materials, and collected data. There is always a gap of some unknown size, a space between the general conditions for the application of existing models and the actual conditions, between the generalities of theories and best practices, and the particulars of the experiment at hand in the present moment.

The space of metaphor, the space between the familiar and the unfamiliar, is filled with the "light, bright ether" that Cassirer speaks of (see previous section). It is the same space indicated by Kuhn's questions, "How does mathematics attach to the world?", "How do our concepts attach to the world?" and, "How does language attach to things?" Though devils lay in wait in the particular details, at root the answer is the same: the attachment between math and world, language and thing, and IUPAC definitions 2 and 1, is metaphorical. But what does *that* mean? Cassirer's idea of *radical metaphor* captures this question in its primal instance, i.e., *the first utterance of a word*:

> Indeed, even the most primitive verbal utterance requires the transmutation of a certain cognitive or emotive experience into sound, i.e., into a medium that is foreign to the experience, and even quite disparate; even as the simplest mythical form can arise only by virtue of a transformation which removes a certain impression from the realm of the ordinary, the everyday and profane, and lifts it to the level of the "holy," the sphere of mythico-religious "significance." This involves not merely a transference, but a real *μεταβασισ εισ αλλο γενοσ*; in fact, it is not only a transition to another category, but actually the creation of the category itself. (Cassirer 1923/1953, 87–8)

Cassirer's reconfigures the discussion of metaphor in this passage. His thoughts about the creativity of what he calls "genuine *radical* metaphor" closely resemble what Whitehead, Kuhn, Harre and Hesse have noted as the creative function, specifically the *knowledge creation* function of metaphor. This conception goes beyond the standard ways of mapping the terms, or concepts, of an analogy or analyzing a metaphor's transference of properties between categories.[22] Interesting, fruitful and popular as semantic- and logic-mapping exercises are, we have something new here. Cassirer draws attention to radical metaphor's *creation* of new categories.

In seeking radical metaphor in the human urge toward symbolic expression, Cassirer found the unbridgeable space between experience and language. This gap is the source and scene of radical metaphor. In this "empty" space, to which neither language nor thought can lay claim, is the *originary* experience that Whitehead was so interested in. The creativity that an individual is capable of, the true novelty of the as-yet-unspoken, lurks in the "wilds of so-called 'empty space'" (Whitehead 1929, 199). By "empty" Whitehead meant space that is empty of the ordering activity of (human and non-human) agents; this "interstitial" space is where he locates consciousness. While consciousness relies on (more or less) stable chemical cycles they do not merely replicate patterns but take advantage of the order and energy they generate and maintain. This is where Whitehead sought the ultimate potential for spontaneity (Whitehead 1929, 105–6).

[22] As found for example in Lakoff and Johnson (2008).

Just as the spontaneity and novelty of consciousness depends on the regularity and stability of physics and chemistry, so too thought relies upon the stability of language and cultural norms. Thought is partly dependent and constrained by language but it grows and thrives by altering these constraints through the creation of new words that redefining the old by recasting them in connection with other players, other contexts of interaction. Scientific knowledge is necessarily constrained by vast networks of vocabularies, categories, procedures, algorithms, models, instrument, data, etc. Nevertheless, knowledge continues to grow because scientists design experimental conditions and induce data to which the network of the known may not apply very well, or at all. On such occasions scientists must improvise activities based on partially applicable existing models. Improvisation takes the form of metaphorical and instrumental incursions into the unknown. Boyle knew this, and MacDonald sees this as part of normal life in a research lab: metaphors, analogies and models are retained only so long as they work to achieve well-articulated goals identified by the changing norms, standards and challenges of disciplinary cultures. One such goal is publication.

Graves recounts that the original draft of MacDonalds article was rejected and reviewers offered suggestions for collecting additional data. Rather than running the experiment again in order to obtain new data, MacDonald presented a different selection of data previously gathered. MacDonald coupled his additional data with citations of data and theories about the photoconductivity of similar amorphous semiconductors. Graves analyzed the manner in which MacDonald used metonyms to make claims about structure on the basis of the semiconductor's behavior under various conditions.[23] In this case, which is by no means uncommon in scientific literature, select processes were made to stand for structures whose existence the peer reviewer initially contested but finally accepted. The phenomena and actual entity under discussion, i.e., photoconductivity in an amorphous semiconductor, did not change between the prepublication draft and the published version: in both phases, MacDonald tried to establish the existence of a specific kind of structure for the photoconductive thin film they had generated using the IBAD process in their lab. Graves analyzes shifts in reasoning and presentation of ideas surrounding the manufacture and testing of the a-SiN_x. Graves' summary of the process asserts that the team

> pursued a cyclical process of collecting measurements. . ., conjecturing about the process (es) that yielded those measurements, and pursuing various explanations for the physical structure suggested by the combination of data and theory. Through this complex process, they derived evidence of the existence of particular characteristics such as structural properties or flaws in the a-SiN_x. However, the movement, back and forth between real entities and proposed theoretical concepts and processes often blurred the boundary between what was real and what was theoretical. (Graves 2005, 193)

Graves here conflates "real" with "data." This conflation indicates her tacit commitment to a metaphysical realism that is at odds with the various alternatives

[23] Metonymy is a specific kind of metaphor that makes a part, or aspect, stand for the whole e.g., saying "friends, Romans, countrymen, lend me your ears."

to realism she ably discusses in her book. Similarly, the "blurring of the boundary" refers to a hard boundary that is only there if one accepts the "standard view" philosophy of science distinctions between theoretical and empirical. Similarly, her invocation of boundary indicates buy-in to the demarcation of the standard view's "context of justification" vs "context of discovery" distinction, a distinction whose absoluteness was successfully challenged over 50 years ago by philosophers and sociologists of science.

There is a significant difference between theory and data, but it is better characterized not as blurring, but as interaction: a mutual interdependence that varies according to discipline, experimental setting and context. Decades of research on the actual practice of science has sharpened the focus on the relationship between data and theory: the relationship is a blur to the extent players have not articulated the dynamics of their interaction. Neither Graves nor MacDonald is a philosopher, so their use of philosophical terms pertaining to science are not always consistent. However, this does not diminish the value of their collaboration and documentation of an inquiry process that extends from a statement of research goals to final publication of experimental research. Graves has demonstrated that the blending of data, theory, model, interpretation and rhetoric occurs with some degree of deliberation at every step. Regardless of the specific rhetorical theory one may subscribe to, and regardless of which kind of realist or non-realist philosophy one favors, it is clear that the practice of science involves tacit and fluctuating commitments to both. Nowhere is their oscillation more explicit than in chemistry's bimodal definition of element.

9.7 Conclusion

Metaphor is not merely linguistic; it can also be deployed as a conceptual strategy that disrupts fixation on any one of two or more explanatory frames that it brings together. In the latter capacity, it enables thought to get on with the important business of innovating something beyond the existing consensus on what, for example, *is* an element, whether basic or simple; what *is* bonding; structure; shape; etc. For example, Rom Harré has elaborated[24] the concept of natural properties to express the notion of contingent, dispositional properties that are especially in evidence in the practice of chemistry.

> The substance-attribute metaphysics immanent in the chemistry of the past must give way to metaphysics of spatially and temporally distributed causal powers to do justice to the way chemistry now appears. The language of the foundations of chemistry must be a language of tendencies and dispositions. (Harré 2010, 110)

Harré's examination of what he calls "chemical vernacular", as opposed to the specialized language of philosophers writing about chemistry, reveals a consistent reliance on causal power of particular agents. Harré calls for better alignment

[24] Harré 2010, Causal concepts in chemical vernaculars. *Foundations of Chemistry* 12:101–115

between the abstractions of the philosophy of chemistry and the concrete vernacular of chemical practice. Effective metaphors modify the behavior of chemists toward a given substance or reaction system by distributing attention among the several dispositional properties that pertain to a given experimental situation, depending on the instrumentation and observational conditions used. The late-twentieth century wave of science studies tend toward Pickering's idea that something like a "mangle of practice," the mutual resistance and accommodation of theory, instrumentation and practice, applies to all contemporary sciences. Over three and a half centuries ago, chemistry emerged by acknowledging and wrestling with this dynamic interdependence to create a seemingly endless list of materials and processes. It should be no surprise then, given the role of metaphor in scientific creativity, that chemistry has been literally the most creative of the sciences.

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Chapter 10
From Corpuscles to Elements: Chemical Ontologies from Van Helmont to Lavoisier

Marina Paola Banchetti-Robino

10.1 Introduction

From a philosophical point of view, one of the more significant changes in chemical ontology from the late sixteenth to the mid-eighteenth century is the shift from a vitalistic conception of fundamental corpuscles, to a mechanistic atomism, to an operational notion of chemical elements. This essay proposes to discuss some of the key figures in this ontological shift, focusing on the ideas of van Helmont, Sennert, Gassendi, Boyle, and Lavoisier. The essay will examine the relationship between the work of late sixteenth century chymists and that of the mechanistic atomists to illustrate the fact that the atomistic framework of the late seventeenth century was intimately dependent upon the earlier work of vitalistic corpuscularian alchemists and chymists.[1] Several mechanistic thinkers, in fact, deplored the revival of atomism because they understood its relationship to the vitalistic chemical philosophy. They worried that this phenomenon might present "an incipient danger to the new mathematically oriented science. The favoring of innate powers within the atoms, corpuscles, or seeds of substances came to distinguish this chemical influence from the work of physically oriented natural philosophers later in the century."[2] As this paper will point out, although modern Epicurean atomism rejected all vitalistic conceptions of matter, mechanistic natural philosophers such as Boyle retained some key concepts of Paracelsian and Helmontian chemical philosophy, while rejecting others. The mechanistic natural philosophers, thus, were "neither 'ancients' nor 'moderns' but rather eclectics who consciously relied

[1] Debus (1977), pp. 545–547.

[2] *Ibid.*

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on their chemical heritage when they found it useful."[3] In addition to tracing the influences of vitalistic corpuscularianism on the shift to a mechanistic atomistic ontology, this paper will also establish historical antecedents for Lavoisier's operational and analytical definition of chemical element, in the work of Sennert and Boyle. As Rocke has pointed out, "the operational criterion of elementarity gradually insinuated itself into the consciousness of chemists, so that by the time Lavoisier first clearly and unambiguously stated it in his classic *Traité élémentaire de chimie*, it could provoke but little controversy."[4]

10.2 The Vitalistic Corpuscularianism of Van Helmont and Sennert

Vitalism has been generally regarded as the view that 'vital forces' or 'vital spirits' are causally operative in nature. Vitalistic descriptions of natural phenomena tend to be qualitative, and vitalistic processes tend to be viewed as holistic and teleological. In the fifteenth and sixteenth centuries, however, it was not unusual to find alchemists and chymists embracing both a vitalistic conception of nature and a corpuscularian conception of matter. In fact, not only is corpuscularianism perfectly compatible with a vitalistic conceptions of nature, but one finds that corpuscularian matter theory actually predates the advent of the mechanistic philosophy and of modern Epicurean atomism. There was, thus, no tension between endorsing a particulate theory of matter along with a belief in the *tria prima*, substantial form, seminal reasons, and vital spirits. In fact, one of the central issues for fifteenth and sixteenth century alchemists and chymists was precisely how to interpret 'vital spirits'. By the end of the sixteenth century, the interpretation of vital spirits becomes unambiguously chemical, while still retaining the strong Neoplatonic tone that it had acquired in the work of Paracelsus, Girolamo Fracastoro, Isaac Beeckman, and Sebastien Basso. Although Joseph Duschene and Oswald Croll reinforce this interpretation when they state that "the only active remedies [are] those prepared by using spirits extracted by distillation",[5] such an unambiguously chemical interpretation of vital spirits is even more evident in the chemical philosophy of Jan Baptista van Helmont (1579–1644). As we shall see presently, there is a strong relationship between van Helmont's theory of vital spirits and his corpuscularian theory of matter. For van Helmont, vital spirit (*Archeus*) is conceived as an alkaline volatile salt that moves through the body and that is "generated from the volatile salt contained in *cruor* [blood without spirit] and by means of a local ferment."[6] The notion of ferment links van Helmont's theory of vital spirit to

[3] *Ibid.*

[4] Rocke (1984), pp. 4–5.

[5] Clericuzio (1994), p. 53.

[6] *Ibid.*

his corpuscular conception of matter. In fact, van Helmont develops an interesting hybrid theory by combining corpuscular and physicalistic explanations of many chemical phenomena with certain aspects of Paracelsian vitalism.[7]

Pre-Helmontian natural philosophy had tended to distinguish between the notion of *minima naturalia* and that of *semina rerum*. This distinction, which dates at least as far back as late antiquity, conceives of *minima naturalia* as the smallest particles of nature that are not further reducible to other particles. By interpreting the notion of *minima naturalia* as the minimum-sized particles of reagents, many Medieval and Renaissance alchemists had developed their own type of corpuscularianism or particulate matter theory, called 'alchemical atomism', as a qualitative version of classical atomism. The Neoplatonic notion of *semina rerum*, on the other hand, was interpreted as referring to spiritual archetypes in nature. Augustine referred to these as 'seminal reasons' (*logoi spermatikoi*). In general, natural philosophers tended to embrace either one or the other of these notions but not both, since one was entirely physicalistic while the other was spiritualistic. Unlike his predecessors, however, van Helmont embraces both the concept of *minima naturalia* and of *semina rerum*, since each concept plays a distinct role in his chemical philosophy. Van Helmont follows Paracelsus in interpreting *semina rerum* as "the main agent in nature [and as] spiritual non-corporeal entities."[8] He believes that *semina rerum* account for non-mechanical properties in nature, while the *minima naturalia* are regarded in strictly physical terms as corpuscles. In fact, "Helmontian atoms are identical with the *minima naturalia*, i.e., the smallest particles into which a substance may be divided. There is little doubt that for van Helmont *minima naturalia* are actual physical units. [However it] is also apparent that they have qualitative determinations, not mechanical properties."[9] According to him, the *semina* work together with the *minima* to bring about changes in nature by providing the spiritual force of action that brings about qualitative chemical alterations.

Van Helmont rejects the explanatory value of strictly mechanical explanations. He claims that in order to provide a mechanical explanation for chemical alterations such as, for example, the mixture of substances, one would have to restrict oneself to considering only the mechanical properties of shape, size, and motion. Under such a mechanistic model, a mixture of substances would have to be explained as the juxtaposition of physical parts. Van Helmont's understanding of what is entailed by mechanical explanations describes precisely the kind of structural chemistry later developed by Boyle to account for analysis and synthesis in strictly mechanical terms. According to van Helmont, however, a "purely mechanical juxtaposition of [physical] parts does not bring about a real mixture [of substances]",[10] because a physical juxtaposition does not bring about a true

[7] Banchetti-Robino (2011), pp. 173–186.

[8] Clericuzio (2000), p. 56.

[9] *Ibid*.

[10] *Ibid*, pp. 58–59.

synthesis. Therefore, strictly mechanical principles cannot adequately explain chemical reactions. Instead, van Helmont claims that chemical reactions, mixtures of substances, and transmutations depend upon ferments that are contained in *semina rerum*, which are the formative principles from which all natural bodies originate. These ferments are themselves formative spiritual agents and, although chemical analysis and the "reduction of bodies into their *minima partes* is a 'pre-condition' for transmutation – [this] is ultimately a spiritual process."[11]

Van Helmont explains many physical changes in this manner, such as the production of gases for example, and he interprets these changes as involving "the disposition of the *tria prima* [salt, sulphur, and mercury] within the corpuscles of water [. . .] The purely material change, that is the attenuation of water parts into atoms, is preliminary to a process that is qualitative, not mechanical."[12] Another example is his corpuscular explanation of certain chemical reactions, such as the 'transmutation' of iron into copper and the production of glass,[13] since "both [chemical reactions] are explained in terms of addition and subtraction of particles. The notion of atoms is also employed in van Helmont's theory of mixture and generation [. . .] [However, van Helmont] imposed severe restrictions on the corpuscular theory of matter. *Semina rerum* and ferments are the active principles on which all natural phenomena ultimately depend."[14] Thus, although the physical change takes place in the *minima naturalia*, the active agents of the chemical change that ensues are the *semina rerum*. As a Paracelsian, van Helmont retains a classical conception of 'element', although he does not accept Aristotle's four elements but only considers air and water to be elements. He does not consider fire as an element and argues that, since earth can be reduced to water, it is also not an element. Nevertheless, van Helmont is a transitional figure in the movement from alchemical principles to chemical elements, and one can understand his notion of *semina rerum* and *minima naturalia* as having an 'elementary' function in chemical explanations. The *minima naturalia* are physically elementary, since they are the simplest material parts of which chemical substances are constituted, while the *semina rerum* are spiritually elementary in that they are the active 'elementary' principles for chemical reactions. With this nuanced ontology, van Helmont makes significant contributions to the development of the early modern corpuscular theory and the theory of elements, although it is important to remember that his corpuscularianism remains vitalistic, to the extent that the non-mechanical principles of the *semina rerum* are required to explain chemical reactions.

Despite its close ties to Medieval and Paracelsian alchemy, van Helmont's work goes far beyond that of Paracelsus and other predecessors. He goes further than his predecessors, insofar as he uses quantification as a tool for research and brings to bear the observational evidence gathered in his own laboratory research to support

[11] *Ibid*, p. 60.
[12] *Ibid*, pp. 57–58.
[13] *Ibid*, p. 56.
[14] *Ibid*, pp. 58–61.

the central claims of his chemical philosophy.[15] Additionally, van Helmont's importance in the context of chemical ontology goes further inasmuch as he takes one of the first steps towards the naturalization of chemical explanations, by employing the notion of a physical particle as the object of change. Although his explanations are not entirely physicalistic and naturalistic, van Helmont significantly contributes to the naturalization of chemical ontology and of chemical philosophy and, thus, towards its modernization.

Before we examine the fully mechanistic seventeenth century Epicurean atomism, it is important to discuss the work of Daniel Sennert (1572–1637), who serves as a significant transitional figure between the work of van Helmont and that of the mechanistic atomist, Pierre Gassendi. As early as 1619, Sennert embraces a theory that mediates between a strictly Aristotelian and a strictly Democritean conception of matter. Sennert believes, like Democritus, that all things are made of atoms but he also believes that atoms are endowed with substantial forms. Thus, although Sennert adopts an atomic theory of matter, he believes that atoms are not simply mechanical in nature but associates them with "formative forces in a sense similar to the *archei* of Paracelsus"[16] and of van Helmont. One of the aspects of Sennert's work that influences the later development of chemistry, however, is his operational notion of substances as "the limits attained by the analytical methods of the laboratory."[17] Sennert appropriates this 'negative-empirical concept', as Bensaude-Vincent and Stengers have called it,[18] from the tradition of Scholastic alchemy.

This negative-empirical concept acquires particular explanatory significance in the context of one of Sennert's most influential experimental procedures, the reduction to the pristine state. For this experiment, Sennert employs nitric acid to separate silver from an alloy of silver and gold,[19] and he describes the results of this procedure as follows: "If gold and silver melt together, they are so roughly mixed per minima that the gold cannot in any way be detected by sight, but if aqua fortis is then poured on, the silver is so thoroughly dissolved that no metal can be detected in the water by sight. But since it is really present, it can emerge thence in segregated form, and certainly in such a way that both the gold and the silver retain their own nature."[20]

> The empirical basis of [Sennert's] atomistic assertion is easily grasped. First, and most important, the silver has been so thoroughly combined with the gold and then dissolved by nitric acid that it is no longer perceptible. And yet, despite having been subjected to one of the most powerful agents of analysis available in the seventeenth century, the metal can be regained intact by means of precipitation. From the perspective of the 'negative empirical' principle, it is therefore operationally *a-tomos* – indivisible – since it has resisted all efforts at laboratory decomposition into its components. Second, the precipitated silver particles

[15] Debus (1977), p. 327.

[16] *Ibid*, p. 192.

[17] Newman (2006), p. 97.

[18] Bensaude-Vincent and Stengers (1996), p. 37.

[19] Newman, p. 99.

[20] Sennert (1619), p. 32.

> are so small that they satisfy another canonic criterion of atomism – the requirement of minute size. In his later works, Sennert would underscore the minuteness of the silver atoms by passing them through filter paper before their precipitation from the acid-silver solution.[21]

According to Sennert, although corpuscles are elementary, the observable qualities of different substances are due to corpuscular aggregations that he considers as atomic species. These atomic species are not elementary but have specific chymical properties that are observable at the macro-level. When the structural arrangement of the elementary corpuscles is altered, the new aggregations form different atomic species with different chymical properties. Sennert's ideas here are prescient in that they anticipate the structural chemistry later to be developed by Robert Boyle. Despite their prescience, however, Sennert's ideas clearly retain a close association with Paracelsian alchemy and Helmontian chymistry. For example, Sennert believes that affinity and, very rarely, antipathy play an important role in the dissolution and precipitation of substances. As Newman points out, Sennert's work shows "the interplay between the two types of qualitative explanation [. . .] the structural and the substantial [. . .] Sennert uses a generalized microstructural explanation in combination with chymical properties originating in the substantial form to explain the origin of a macrolevel effect."[22] Sennert attempts to replace the notion of the Aristotelian elements with the notion of corpuscles endowed with substantial form, but he realizes the empirical difficulty associated with positing any kind of substantial form. "The substantial form itself is completely insensible, a causal *terminus post quem*, from which perceptible qualities arise without revealing the nature of their source. Substantial form, therefore, is a sort of 'black box' from which qualities emerge. The unknowable nature of Sennert's substantial form is an Aristotelian empiricist's statement of nescience."[23] Ultimately, neither the Aristotelian nor the Sennertian notion of substantial form could be sustained within chemical explanations, and one of the central aims of mechanistic chemical philosophy was to provide a heuristic alternative to this empirically problematic Scholastic notion.

10.3 The Mechanistic Corpuscularianism of Gassendi and Boyle

Before I begin the discussion of mechanistic atomism and its indebtedness to vitalistic corpuscularianism, I will give a general account of the basic tenets of the mechanistic philosophy. 'Mechanism', or the mechanistic philosophy, is the view according to which matter is inert and all interactions in nature are produced

[21] *Ibid*, pp. 99–100.
[22] *Ibid*, p. 136.
[23] *Ibid*, pp. 138–139.

by the impact of particles. In this sense, mechanism is also reductionist in that all qualities (including chemical qualities and reactions) are thought to be ontologically and epistemically reducible to the mechanical and quantitative properties of matter. Mechanism not only embraces reductionism, but it also embraces deducibility, that is, all higher-level phenomena or properties are at least theoretically entirely deducible from lower-level properties. Although the mechanistic philosophy as such gains dominance in the seventeenth century, it inherits its commitment to the deducibility and reducibility of higher-level properties from ancient Democritean and Epicurean atomism. It is, thus, not coincidental that the revival of classical atomism in the seventeenth century occurs hand-in-hand with the development of the mechanical philosophy. Accordingly,

> the physical world is represented by particles of matter in motion and can be interpreted by the laws of motion determined by statistics [. . .] dynamics [and] mechanics [. . .] Natural phenomena such as air resistance, friction, the different behaviors of individual bodies, the qualitative features of the physical world were now considered irrelevant to the discourse of natural philosophy or viewed as disturbing circumstances which were not [. . .] to be taken into account in an explanation of the physical world.[24]

For mechanists, "any explanation of natural events requires the building of a mechanical model as a 'substitute' for the actual phenomena being studied."[25] Mechanistic explanations provided an alternative to the vitalistic and teleological accounts that had dominated natural philosophy up to the sixteenth century, since it assumed that "the explanation of natural phenomena excludes all references to *vital forces* or *final causes*."[26] Since mechanism denied any intrinsic motion or self-organization to matter, it attributed all motion and organization to external causes.

Pierre Gassendi (1592–1655) was, arguably, the strongest proponent of mechanistic Epicurean atomism in early seventeenth century France. From the point of view of chemical philosophy, his *Philosophia Epicuri syntagma* (1649) is significant because it marks the shift from the vitalistic corpuscularianism of van Helmont and Sennert to a mechanistic atomism of the sort later defended by Walter Charleton, Robert Boyle, and Isaac Newton. Gassendi contributes to the acceptance of Epicurean atomism by making this view compatible with Christian theism. He does this by revising classical atomism in important ways. Significantly, Gassendi argues against Epicurus that motion is not inherent to matter and that, therefore, an external cause is required to impress motion upon atoms and this external cause is God. In the *Syntagma philosophicum* (1658), Gassendi claims that matter is that which has dimensions and is capable of resistance, which means that prime matter is constituted of solid and indivisible particles. Thus, unlike Descartes, Gassendi believes that atoms are indivisible corpuscles endowed by God with mass and motion, and he refuses to define atoms as mathematical points since these have no empirical reality. Like Sennert and Boyle, Gassendi believes that "the primordial

[24] Rossi (2001), p. 122.
[25] *Ibid*, p. 125.
[26] *Ibid*.

atoms combine with one another to form compound corpuscles",[27] which he calls 'molecules' (*moleculae*). These molecules are stable, compounded corpuscles that cannot be further analyzed but that serve as intermediaries between indivisible atoms and tangible perceptible bodies. Since they are produced by chemical resolution, these molecules are, in a certain sense, 'elementary' although they are not simple particles. Although this notion will be developed much later in the work of Antoine Lavoisier, it must be stressed that for Gassendi the only true elements are atoms, since they are the only particles that are completely indivisible by natural means. Gassendi believes that there are several intermediary levels of compounded corpuscles between fundamental atoms and concrete bodies, and it is these molecules that compose the traditional chemical 'elements' (sulfur, mercury, salt, earth, water). Thus, the notion of chymical molecules is not incompatible with his mechanistic atomism. Gassendi believes that textural alterations to molecules produce new qualities in substances and that such changes in qualities can be induced by chemical operations.[28] Gassendi suggests that the molecules of chemical principles characterize the various species of bodies, depending on their proportions and composition. He finds it difficult, however, to distinguish homogeneous bodies with identical molecules from mixed bodies, especially when determining the nature of metals.[29]

Gassendi's revision of classical Epicurean atomism to make it compatible with Christianity was crucial to the success of mechanistic atomism in Europe and had a great influence on the work of Walter Charleton (1619–1707). Charleton's work, in turn, was the primary vehicle for the acceptance of mechanistic atomism in England and for the influence of Gassendi's ideas on the work of Robert Boyle (1627–1691). In fact, Boyle is one of the first English scientists to embrace 'purified' Epicurean atomism, as advocated by Gassendi and Charleton, although he adjusts Epicurean theory to make compatible with the Cartesian view. Boyle attempts to bring the atomic and mechanical philosophies within the compass of experiment, and one of the main reasons for Boyle's influence on the Royal Society's acceptance of mechanical atomism was that his experiments were indeed qualitatively and quantitatively superior to those that had been previously performed by other chemists.

What makes Gassendi's revision of classical atomism particularly attractive for Boyle is the insistence that nature should not be treated as an agent. For Boyle, nature is devoid of purpose, volition, and sentience. Material nature, by itself, is inanimate and the only source of agency is God.[30] However, one of Boyle's main heuristic reasons for preferring mechanistic atomism to the theory of substantial form or that of the *tria prima* is that neither of these could serve a satisfactory explanatory function for chemical reactions and changes witnessed in experimental situations. By the mid-seventeenth century, it was evident to natural philosophers

[27] Newman, pp. 191–192.

[28] *Ibid*, p. 192.

[29] Pinet (2004), pp. 67–82.

[30] Shapin and Schaffer (2011), p. 202.

that not every chemical reaction or change involved the active role of salt, sulfur, or mercury in some form. Thus, the notion of the *tria prima* soon lost credibility for chemists such as Boyle. Substantial form, on the other hand, could not provide adequate explanations for the chemical transformations that occurred via analysis and synthesis, in part because such explanations were bound to end in circularity.

If one claims that analysis destroys the form of the substance and that synthesis restores this form, this does not suffice to tell us what this form actually is. If, on the other hand, substantial form is something non-physical that disappears and then reappears, then this does not explain how a chemical procedure can affect a non-physical 'form'. If substantial form simply means the substance itself, then we end up with a circular explanation: The substance has been altered because the substance has been altered. Any of these three choices leaves us epistemically unsatisfied. To be fair, there is another, more interesting way of understanding substantial form that serves as a precursor to Boyle's mechanistic structuralism. Substantial form can be understood as meaning the inner structure that gives the substance its essential properties. The problem with this understanding of substantial form, however, is that it still does not tell us what this inner structure is. Boyle latches on to this idea of inner structure but seeks to understand it in strictly mechanistic and corpuscularian terms, without any reference to substantial form.

Boyle's clearest statement of his theory of matter and of his corpuscularian philosophy is found in *The Origin of Forms and Qualities* (1666). In this work, he takes a position that mediates between Gassendi and Descartes. Against Gassendi and Charleton and in agreement with Descartes, Boyle believes that material corpuscles are not endowed by God with internal energy or 'motive virtue'. Additionally, he agrees with Descartes that material corpuscles are, at least in theory, infinitely divisible. Despite their theoretical divisibility, Boyle agrees with Gassendi against Descartes, that material corpuscles are impenetrable and indestructible by natural means. Matter conserves shape and size and cannot, thus, be reduced to pure geometrical extension. Like visible bodies, insensible corpuscles have the three essential properties of shape, size, and motion. According to Boyle, God furnished the various fundamental corpuscles with various motions and directed their various movements and compositions to form the variety of inanimate and animate bodies that exist.

In this work, Boyle describes corpuscles as *minima naturalia*, that is, as corpuscles that are indivisible by nature, although they are mentally and divinely divisible. These corpuscles form clusters or concretions of various sorts that affect the senses in various ways. Although Boyle does not adopt the Gassendian term 'molecule', he does avail himself of the concept attached to this term. Thus, 'elementary' corpuscles, or elements, are corpuscular aggregations and are considered semi-permanent because they cannot be further analyzed into smaller particles. The structure of these corpuscular aggregations accounts for the chemical properties of substances, which Boyle calls 'essential properties'. Such semi-permanent corpuscles or *minima naturalia* can also be termed 'chymical atoms', as opposed to 'physical atoms' or *prima naturalia*. These chymical atoms are hierarchically secondary with respect to primary corpuscles, but they are primary with respect to mixed

substances. When combined, they form primary mixtures that can, in turn, be combined to form different degrees of mixtures. To the extent that 'chymical atoms' are semi-permanent and homogeneous with regard to their essential properties and that they cannot be altered by chemical procedures, they can be considered as chemically 'elementary'.

As Boas Hall has pointed out, the concept of 'element' changed radically in the course of the centuries[31] and particularly in the period between the sixteenth and the eighteenth centuries. Boyle's work signals precisely such a change in how elementary substances are conceptualized. To the extent that he accepts the conventional seventeenth century definition of elements as "substances necessarily present in all bodies",[32] Boyle rejects the existence of such substances and recognizes only "corpuscles [as the minutest portions of matter present in] all bodies, including those [bodies] regarded by others as elementary."[33] For him, what other chemists call elements are actually concretions of primary corpuscles. However, as mentioned above, Boyle does employ the notion of 'chymical atom', which he inherits from Sennert, to refer to those concretions of primary corpuscles that retain their deep microstructure through analysis by fire or chemical corrosives.[34] 'Chymical atoms' are, for him as for Sennert, the final products of chemical analysis. Thus Boyle, like Sennert before him, endorses an operational conception of 'chymical atom' and of 'elementarity' that anticipates the important work to be done later by Lavoisier.

This operational notion shows Boyle moving beyond Gassendi, Charleton, and Descartes by not limiting himself to mere philosophical speculation about the most fundamental particles of matter and, instead, attempting to link his claims about microstructure to the actual results of empirical analyses in the laboratory. Unfortunately, however, there is a problem in Boyle's notion of microstructure that cannot be resolved by the mechanical philosophy. Boyle's notion of structure is a strictly geometrical concept. Although Boyle claims that the deep structure of 'chymical atoms' cannot be altered by analytical corrosives or fire, he never gives an account of how and why this deep structure persists even under analysis by the most powerful tools available to the chemist in his time. Since the concept of chemical bond did not yet exist and would have been anathema to the mechanical philosophy, the resistance of deep structure to chemical analysis remains unexplained. Thus, Boyle fails to give a satisfactory account of the operational irreducibility of semi-permanent 'chymical atoms'.

Additionally, given the lack of technologies available to early modern chemists, any possible link that could be forged between microstructure and experimental findings were tenuous at best and did not warrant the assumption that either atoms or fundamental corpuscles were involved at the micro-level. Thus, seventeenth

[31] Boas Hall (1968), p. 21.
[32] *Ibid*, p. 27.
[33] *Ibid*.
[34] Anstey (2011), p. 21.

and eighteenth century atomism remained a primarily speculative attempt at conceptualizing the fundamental nature of matter. Even Newtonian atomism failed to provide a satisfactory atomic theory that could serve as a foundation for experimental predictions of chemical phenomena. Newton did refine early modern atomism by introducing force as the means of interaction between particles. However, although the notion of forces of interaction provided a theoretically superior account of the relation between particles than the geometrical microstructure posited by Boyle, Newton still conceived of atoms in much the same manner as Boyle had conceived of primary corpuscles. Newton's conception of atoms as the most minute and impenetrable particles of matter is as speculative as earlier attempts at conceptualizing elementary particles. Thus, as the century progressed, it became increasingly clear that speculative atomism, whether vitalistic or mechanistic, "offered little [that was] of practical utility to chemists"[35] and that they could easily dispense with these types of theories regarding the fundamental nature of matter.

10.4 Lavoisier's Rejection of Corpuscularian and Atomistic Theories

It is against this background of eighteenth century skepticism regarding speculative theories of matter that the ideas of Antoine Lavoisier (1743–1794) must be contextualized. A fundamental aspect of Lavoisier's work was his rejection of 'metaphysically suspect' corpuscularian and atomistic ontologies in favor of a taxonomy of operationally defined chemical elements. For Lavoisier, the chemical element is no longer the completely indivisible corpuscle (the philosophical atom) or the 'chymical atom' that is difficult to analyze by natural means. It is, instead, that substance that remains as the last product of analysis. In the preface to his *Traité Élémentaire de Chimie* (1789), Lavoisier explains the general principle that he proposes to apply in his chemical studies. He states, "just as in a child, it is ideas that are the product of sensation, it is sensation that gives birth to an idea, so it is for that individual who begins to undertake the study of the physical sciences: Ideas must only arise as a consequence, as an immediate result of, an experience or a sensation."[36] For Lavoisier, since correct ideas can only arise from experience, a priori notions that are contrived by the imagination or by the faculty of reason unchecked can lead us into serious scientific error. To avoid such errors, claims

[35] Hendry (2006), p. 865.

[36] "De même que dans l'enfant l'idée est un effet de la sensation, que c'est la sensation qui fait naître l'idée; de même aussi pour celui qui commence à se livrer à l'étude des science physiques, les idées ne doivent être qu'une conséquence, une suite immédiate d'une expérience ou d'une observation." [Lavoisier, Antoine-Laurent, *Traité Élémentaire de Chimie*, Vol. 1 (Paris: 1789), p. viii].

Lavoisier, "I have imposed upon myself the rule of proceeding only from the known to the unknown, [and] of deducing no consequence that does not immediately derive from experience and observation."[37] Based upon these strictly empiricist principles of study, Lavoisier concludes that the positing of suspect metaphysical entities, such as Boyle's corpuscles or Newton's atoms, is scientifically unacceptable since it does not advance but, rather, hinders our empirical knowledge about substances, their behavior, their interaction, and their transformation. Because corpuscles or atoms cannot be measured, weighted, or otherwise empirically studied, their postulation contributes nothing to experimental work or to empirical chemical knowledge.

In order to steer clear of metaphysical speculations about the ultimate nature of matter, Lavoisier avoids any reference to atoms or to minutest particles of matter and proposes, instead, "a reformed nomenclature for chemistry, in which the names of compound substances would reflect their elementary composition".[38] In fact, he regards the decomposition of material bodies into the substances of which they are composed as the chief aim of chemistry. Ultimately, however, this proposed reform of the nomenclature of compound substances in terms of their elementary composition forces the question of what is to be regarded as an 'element'. Lavoisier proposes to answer this question by restricting himself to what can be ascertained by strict empirical means. He explains that, "[i]f by the name of element, we mean the simple and indivisible molecules that compose bodies, it is probable that we do not know them: if, on the contrary, we attach to the name of element or principle of bodies the idea of the last point at which analysis arrives, all of the substances that we have not yet been able to decompose by any means are, for us, to be considered elements."[39]

For Lavoisier, this 'analytical definition' of element as a 'simple substance' serves "to supplant [any] a priori metaphysical speculation about the ultimate principles of which things are made."[40] This operational definition provides a criterion for deciding when a substance should be regarded as an element but it does not tell us *what* the term 'element' means.[41] In fact, Lavoisier admits that the table of elements that he derives by applying this notion is entirely open to revision. He admits that those substances that are regarded as simple could, at some time, be

[37] "[J]e me suis imposé la loi de ne procéder jamais que du connu à l'inconnu, de ne déduire aucune conséquence qui ne dérive immédiatement des expériences & des observations." [Lavoisier, Antoine-Laurent, *Traité Élémentaire de Chimie*, Vol. 1 (Paris: 1789), pp. x–xi].

[38] *Ibid*, p. 866.

[39] "Si par le nom d'élémens, nous entendons désigner les molécules simple & indivisibles qui composent les corps, il est probable que nous ne les connoisons pas: que si au contraire nous attachons au nom d'élémens ou de principe des corps l'idée du dernier terme auquel parvient l'analyse, toutes les substances que nous n'avons encore pu décomposer par aucun moyen, sont pour nous des élémens." [Lavoisier, Antoine-Laurent, *Traité Élémentaire de Chimie*, Vol. 1 (Paris: 1789), p. xii].

[40] Hendry (2012), p. 66.

[41] *Ibid*.

discovered to be compound substances. However, since the means for analyzing these substances further do not exist during his time, one must not assume them to be composed until observation can prove otherwise.

As mentioned earlier, Lavoisier's operational conception of element is not entirely new to him, as it finds echoes the work of Sennert and Boyle. Additionally, Lavoisier makes a conceptual distinction, very similar to that of Boyle, between fundamental particles and the unanalyzable substances of the laboratory. However, because there is no empirical way to link fundamental particles with chemical elements, Lavoisier refuses to make "any connections between atoms and elements [for there is], philosophically, a profound distinction between them."[42] Because Lavoisier wishes to apply a systematic and entirely empirical method to chemistry and to incorporate the chemical evidence of the laboratory into a quantitative system based upon the weights of substances, "chemical analysis and weighing go hand in hand [. . .] Chemical theories based on anything other than experimental evidence [and quantitative measurement] are simply worthless, and that [goes] for every theory of the elements [. . .] that had been proposed by his predecessors."[43] Following Lavoisier's pronouncements against metaphysical speculations in chemistry, no atomic theory could garner credibility unless it could link the notion of atom to quantifiable empirical and experimental data. The development of such an empirical and quantitative atomic theory, however, would not occur until the early nineteenth century and the work of John Dalton, whose ideas will not be discussed here as they are far beyond the scope of this essay.

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[42] Levere (2001).

[43] *Ibid*, p. 80.

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Chapter 11
Mendeleev and the Rare-Earth Crisis

Pieter Thyssen and Koen Binnemans

A few years ago, C. H. Evans noticed that historically "the rare-earth elements [had] created theoretical, as well as practical, headaches for chemists", but he admitted that "none [had been] greater than their proper position in the periodic table".[1] According to Evans' opinion, "the interplay between Mendeleev's periodic system and the rare-earth elements is an interesting one, worthy of deeper analysis by future scholars."[2] Following this suggestion, the substance of this paper will focus on Mendeleev's attitude towards the problematic accommodation of the rare-earth elements in the periodic system during the period 1869–1871. Henceforth, the term *rare-earth crisis* will be used to denote this accommodation issue.

There has been relatively little mention of the rare-earth crisis in the scholarly literature on Mendeleev and his periodic system. One notable exception is provided by the work of the Russian historian, D. N. Trifonov, who wrote two books on this subject-matter in Russian. Within the English scholarly literature, however, not much material is to be found. And yet, as will be argued in this paper, the rare-earth crisis embodied one of the greatest threats to the periodic system—endangering some of the most cherished beliefs of Mendeleev.

Mendeleev himself referred to the rare earths as *podvodnyi kamen* (or *underwater stone*), also translated as 'stumbling block'.[3] This evocative term already hints to what extent the placement of the rare-earth elements had troubled

[1] Evans, C. H. "The Discovery of the Rare Earth Elements." *Chemistry in Britain* (1989): 880–882. (page 881)

[2] "Introduction." In *Episodes from the History of the Rare Earth Elements*, ed. C. H. Evans, xviii. Dordrecht/Boston/London: Kluwer Academic Publishers, 1996.

[3] The authors thank M. Gordin for bringing this to our attention.

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Mendeleev. After his discovery of the periodic system in February 1869, Mendeleev tirelessly laboured at the clarification, illustration, refinement, and optimisation of his periodic classification of the elements. Not surprisingly, the accommodation of the rare-earth elements formed an important part of Mendeleev's research program, which lasted approximately 2 years—from 1869 till 1871. But at the end of 1871, Mendeleev threw in the towel, distancing himself from the various discussions concerning the placement of the rare earths which were held at the end of the nineteenth century.

Notwithstanding the fact that Mendeleev failed to resolve the rare-earth crisis, he definitely grasped the essence of the subject-matter better than any other chemist at the time. More importantly, the rare-earth elements also played a key role in inducing a number of important changes in Mendeleev's deep, almost philosophical, viewpoints with regard to the *epistemological concept of a chemical element* and the *nature of elementary groups*. The unexplainable properties and mystifying character of most rare earths made him question the current definition of a chemical element, as well as the validity and universality of the periodic law, and even led Mendeleev into hypothesising about the internal structure of matter and constitution of atoms.

The aim of this research paper is twofold: First of all, the early history of the accommodation of the rare-earth elements in the period 1869–1871 will be retraced. Secondly, and most importantly, the principal content of this paper intends to clarify some of Mendeleev's perceptions about primary and secondary groups, the elements as basic and simple substances, and the use of short and long form tables.

Since Mendeleev's viewpoints underwent some crucial changes around the second half of 1870, our historical argumentation will be built around two sections. The first section (Sect. 11.1) centres on the period from Mendeleev's discovery in February 1869 till the end of the first half of 1870. The second period which extended from the second half of 1870 to the end of 1871 will be dealt with in the second section (Sect. 11.2). A summary of our principal conclusions can be found in Sect. 11.3.

11.1 The Period 1869–1870

11.1.1 A Septuplet of Homeless Elements

Nearly 150 years ago, on the 17th of February 1869,[4] a pamphlet was printed with the aim of circulating it among the most distinguished Russian and European

[4] All events in Russia are dated according to the Julian calendar (Old Style), which was used in Russia until January 1918. It lagged 12 days behind the Gregorian calendar (New Style) in the nineteenth century, and 13 days in the twentieth. For example, February 17, 1869 (Old Style) corresponds to March 1, 1869 (New Style), as can be seen on Fig. 11.2. Gregorian dates will be given for all events occurring outside Russia.

ОПЫТЪ СИСТЕМЫ ЭЛЕМЕНТОВЪ.

ОСНОВАННОЙ НА ИХЪ АТОМНОМЪ ВѢСѢ И ХИМИЧЕСКОМЪ СХОДСТВѢ.

			Ti = 50	Zr = 90	? = 180.	
			V = 51	Nb = 94	Ta = 182.	
			Cr = 52	Mo = 96	W = 186.	
			Mn = 55	Rh = 104,4	Pt = 197,1.	
			Fe = 56	Ru = 104,4	Ir = 198.	
			Ni = Co = 59	Pl = 106,6	O = 199.	
H = 1			Cu = 63,4	Ag = 108	Hg = 200.	
	Be = 9,4	Mg = 24	Zn = 65,2	Cd = 112		
	B = 11	Al = 27,1	? = 68	Ur = 116	Au = 197?	
	C = 12	Si = 28	? = 70	Sn = 118		
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210?	
	O = 16	S = 32	Se = 79,4	Te = 128?		
	F = 19	Cl = 35,6	Br = 80	I = 127		
Li = 7	Na = 23	K = 39	Rb = 85,4	Cs = 133	Tl = 204.	
		Ca = 40	Sr = 87,6	Ba = 137	Pb = 207.	
		? = 45	Ce = 92			
		?Er = 56	La = 94			
		?Yt = 60	Di = 95			
		?In = 75,6	Th = 118?			

Д. Менделѣевъ

Fig. 11.1 An attempted system of the elements based on their atomic weight and chemical analogies. A pamphlet with D. Mendeleev's first periodic system, distributed on the 17th of February 1869

chemists of that time (Figs. 11.1 and 11.2).[5] The flyer was entitled *An Attempted System of the Elements Based on Their Atomic Weight and Chemical Analogies* and was signed by the 35 year old professor, D. Mendeleev (Д. Менделеев), who at that time was holding the chair of general chemistry at the renowned university of St. Petersburg (Fig. 11.3). The whole set of chemical elements had been logically laid down in 6 columns of increasing atomic weight and 19 rows of natural groups,[6] thus constituting the very first embodiment of the *periodic law*.

[5] Mendeleev, D. I. "An Attempted System of the Elements Based on Their Atomic Weights and Chemical Analogies." 1869a. A total of two hundred single page copies were printed—150 in Russian (Fig. 11.1), and another 50 in French (Fig. 11.2). See Krotikov, V. A. "The Mendeleev Archives and Museum of the Leningrad University." *Journal of Chemical Education* 37, no. 12 (1960): 627.

[6] Examples of natural groups (i.e. elementary groups) are the alkaline metals and the halogens.

Fig. 11.2 Essai d'une [*sic*] système des éléments d'après leurs poids atomiques et fonctions chimiques par D. Mendeleeff, professeur de l'Université à Saint-Pétersbourg. The French version of the Russian pamphlet, represented in Fig. 11.1

ESSAI D'UNE SYSTÈME DES ÉLÉMENTS

D'APRES LEURS POIDS ATOMIQUES ET FONCTIONS CHIMIQUES,

par D. Mendeleeff,

protess. de l'Univers. à S-Petersbourg.

			Ti = 50	Zr = 90	? = 180.	
			V = 51	Nb = 94	Ta = 182	
			Cr = 52	Mo = 96	W = 186	
			Mn = 55	Rh = 104,4	Pt = 197,4	
			Fe = 56	Ru = 104,4	Ir = 198	
			Ni = Co = 59	Pl = 106,6	Os = 199.	
H = 1			Cu = 63,4	Ag = 108	Hg = 200	
	Be = 9,4	Mg = 24	Zn = 65,2	Cd = 112		
	B = 11	Al = 27,4	? = 68	Ur = 116	Au = 197?	
	C = 12	Si = 28	? = 70	Sn = 118		
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210?	
	O = 16	S = 32	Se = 79,4	Te = 128?		
	F = 19	Cl = 35,5	Br = 80	I = 127		
Li = 7	Na = 23	K = 39	Rb = 85,4	Cs = 133	Tl = 204	
		Ca = 40	Sr = 87,6	Ba = 137	Pb = 207.	
		? = 45	Ce = 92			
		?Er = 56	La = 94			
		?Yt = 60	Di = 95			
		?In = 75,6	Th = 118?			

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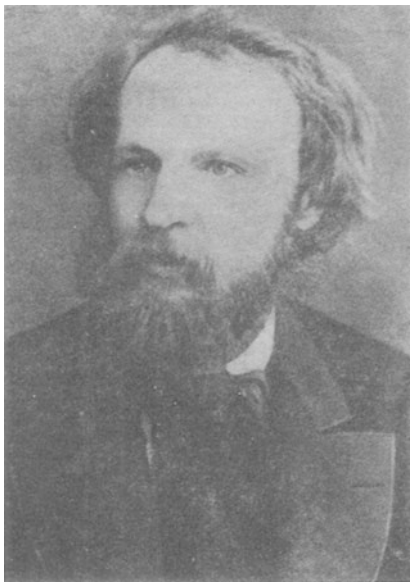
Fig. 11.3 The 35 year old professor of general chemistry, Dmitrii Ivanovich Mendeleev in 1869



As compared to the modern periodic table, the *Attempted System* is rotated 90° clockwise. The periods are lying vertically, rather than horizontally, and similar elements are grouped in horizontal rows, rather than vertical columns. Notice also that the rows of alkali metals and halogens are adjacent to one another (the noble gases were not yet discovered in 1869). Finally, many of the problematical elements are simply grouped on the right-hand side of the table in no particular order whatsoever.

When inspecting Mendeleev's *Attempted System* more closely, one cannot help it to be struck by the following intriguing fact: Normally, when reading from top to bottom, and from left to right, one should obtain an ever increasing atomic weight sequence.[7] It appears however that this sequence gets interrupted twice. First, when passing from In (75.6, third column, bottom row) to Ti (50, fourth column, upper row), and a second time, when moving from Th (118, fourth column, bottom row) to Zr (90, fifth column, upper row).[8] One possible way of restoring the sequence consists in eliminating a total of seven elements from the system—namely Er, Yt, In, Ce, La, Di, and Th.[9] Indeed, if such is the case, the sequence passes from the unknown element with an atomic weight of 45 to Ti with an atomic weight of 50, and from Sr with an atomic weight of 87.6 to Zr with an atomic weight of 90 – in accordance with the gradual increase in atomic weight.

It thus appears that "seven little studied elements remained outside of the table".[10] This septuplet of homeless elements consisted of indium (In), thorium (Th) and the five rare earths—erbium (Er), yttrium (Yt), cerium (Ce), lanthanum (La), and didymium (Di).[11] Question marks and wrong atomic weights reigned in the last rows of Mendeleev's system, and a new place had to be found for the homeless septuplet. We will call this problematic accommodation issue the *rare-earth crisis*.

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[7] It would be scientifically more correct to use the term *relative atomic mass*. In this chapter however, the historical term *atomic weight* will be used throughout.

[8] Notice that the atomic weight sequence is violated two more times by the inversion of tellurium (Te) and iodine (I), and by the insertion of gold (Au) and bismuth (Bi).

[9] Yt is an old symbol for yttrium (Y). Di, on the other hand, was the symbol for the element didymium, which later turned out to be a mixture of praseodymium (Pr) and neodymium (Nd).

[10] Quoted from Brooks, N. M. "Developing the Periodic Law: Mendeleev's Work During 1869–1871." *Foundations of Chemistry* (2002): 129.

[11] It must be remarked that terbium, another rare-earth element, was already known at the time when Mendeleev drew up his first periodic system, but Dmitrii Ivanovich decided to not include this element—following as a matter of fact Bunsen and Bahr's advice. Terbia had been discovered as early as 1843 by Mosander, but Mendeleev was not convinced that he was dealing with a genuine element. He therefore wrote the symbol of terbium (Ter.) in the marginalia of a piece of scrap paper when he was composing the *Attempted System*, but directly underneath this symbol Mendeleev scribbled that "it does not exist according to Bunsen" (не существует по бунзену). In writing this sentence, Mendeleev was in all probability referring to Bahr, J. F., and Bunsen, R. "Ueber Erbinerde Und Yttererde." *Annalen der Chemie und Pharmacie* 137 (1866a): 1–33. See also Bahr, J. F., and R. Bunsen. "Ueber Erbinerde Und Yttererde." *Chemisches Central-Blatt* 11, no. 8 (1866b): 118–125, and Bahr, J. F., and R. Bunsen. "Ueber Erbinerde Und Yttererde." *Zeitschrift fur Chemie* 9 (1866c): 72–77.

11.1.2 Mendeleev's Experimental Research in 1869–1870

Mendeleev published a trilogy of papers during the first period from 1869 till the first half of 1870. His first paper *On the Correlation Between the Properties of the Elements and their Atomic Weights* was drafted in the second half of February 1869 and put forth his *Attempted System* as a useful classification of the chemical elements (Figs. 11.1 and 11.2).[12] During the month of August 1869, Mendeleev wrote a second paper summarising his experimental results *Concerning the Atomic Volumes of Simple Bodies*.[13] He then turned to an investigation of the higher salt forming oxides and presented his results on October 2, 1869 during a meeting of the *Russian Chemical Society* in a paper titled *On the Quantity of Oxygen in Metal Oxides and on the Valency of the Elements*.[14] If his first paper had served to announce the discovery of the periodic law (and secure his priority), the remaining two offered an important illustration (and thus validation) of the concept of periodicity by his comprehensive study of both the physical and chemical properties of the elements.

Notwithstanding the importance of these experimental investigations, none of them was directly aimed at resolving the rare-earth crisis, and the septuplet of elements (Er, Yt, In, Ce, La, Di, and Th) remained outside the system. This does not imply however that Mendeleev wasn't pondering the issue. As will be argued in the following paragraphs, Mendeleev had been working ardently on the problem from a theoretical/philosophical line of approach, and there is much to be learned about the crux of the rare-earth crisis from a careful and meticulous examination of Mendeleev's trilogy of papers.

[12] Mendeleev, D. I. "On the Correlation between the Properties of the Elements and Their Atomic Weights." *Zhurnal Russkogo Khimicheskogo Obshchestva* 1, no. 2–3 (1869b): 35, 60–77. A reproduction of Mendeleev's table appeared in Mendeleev, D. I. "Versuch Eines Systems Der Elemente Nach Ihren Atomgewichten Und Chemischen Funktionen." *Journal für praktische Chemie* 106 (1869c): 251. A more complete abstract of Mendeleev's article can be found in Mendeleev, D. I. "Über Die Beziehungen Der Eigenschaften Zu Den Atomgewichten Der Elemente." *Zeitschrift für Chemie* 5 (1869d): 405–406. See also Mendeleev's supplementary comments, made in autumn 1869, in Mendeleev, D. I. "On the Correlation between the Properties of the Elements and Their Atomic Weights." *Zhurnal Russkogo Khimicheskogo Obshchestva* 1 (1869f): 229–230, and an abstract in Mendeleev, D. I. "Die Beziehungen Zwischen Den Eigenschaften Der Elemente Und Ihrer Atomgewichten." *Berichte der Deutschen chemischen Gesellschaft* 2 (1869g): 553.

[13] Mendeleev, D. I. "Concerning the Atomic Volumes of Simple Bodies." In *Arb. II Kongr. Russ. Ärzt. Naturf.*, 1869e.

[14] Mendeleev, D. I. "On the Quantity of Oxygen in Metal Oxides and on the Valency of the Elements." *Zhurnal Russkogo Khimicheskogo Obshchestva* 2 (1870a): 14–21.

11.1.3 Wrong Atomic Weights and Erroneous Valencies

Due to the recent discoveries of the rare-earth elements, most of their chemical and physical properties were still shrouded in mist at the beginning of 1869, and Mendeleev had to manage with the limited information he had at his disposal. At the time, Mendeleev still adhered to the old Berzelian atomic weights for the rare-earth elements. Not one of these values corresponded to the real atomic weights however, as they were based on the erroneous assumption that most rare-earth elements were *bivalent* instead of *trivalent*.[15] Their oxides were thus represented by the formula RO (with the higher oxide of cerium denoted as R_2O_3).

With the wrong atomic weights at hand, Mendeleev naturally failed to accommodate the rare earths, and he felt obliged to position them at the periphery of his *Attempted System*. If Mendeleev was to accommodate the rare earths properly, he would have to change their valency from 2 to 3. Even though Mendeleev would be the first in proposing this modification of valency number, he only did so at the end of the first half of 1870. Before that time (that is, during the first period from 1869 till 1870), Mendeleev continued to look upon the rare-earth elements as being bivalent and he used the wrong atomic weights throughout.

This notwithstanding, Mendeleev certainly had doubts about the position of the rare-earth elements from the very outset. As he admitted in his 1869 article *On the Correlation between the Properties of the Elements and Their Atomic Weights*:

> With respect to the position of some elements, there exists, quite understandably, complete uncertainty. In particular, this holds for those elements that are little studied and whose correct atomic weight has hardly been established with any certainty. Among these are, for example, yttrium, thorium, and indium.[16]

11.1.4 The Companions of Cerium

When Lavoisier defined a chemical element in 1789, 26 elements were actually known. Eighty years later, at the onset of 1869, a total of 36 elements had been added to the list. More and more chemists consequently felt the need for a systematic organisation. But instead of building a periodic table, as Mendeleev did in 1869, they felt inclined to group together elements with similar physical and chemical characteristics—ending up with a network of small, so-called *natural groups*. Well-known examples were the highly reactive halogens (F, Cl, Br, I) and the silver coloured and water-reactive alkali metals (Li, Na, K, Rb, Cs).

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[15] The atomic weight AW of an element X is related to its valency V via the general formula $AW(X) = EW(X)\ x\ V(X)$, with EW the equivalent weight of X.

[16] Mendeleev, D. I. "On the Correlation between the Properties of the Elements and Their Atomic Weights." In *Mendeleev on the Periodic Law*, *Selected Writings*, *1869–1905*, ed. William B. Jensen, 30. Mineola, New York: Dover Publications, Inc., 2002.

In the same way, Mendeleev recognised the similarity in chemical and physical properties of the rare-earth elements, and considered them to be members of a *natural group* as he proclaimed in his 1869 article. "Only with regard to some *groups of elements* are there no doubts that they form a whole and represent a natural order of similar manifestations of matter", Mendeleev explained. "Such groups are: the halogens, the alkaline earth metals, the nitrogen group, and also—in part—the sulfur group, the companions of platinum, *the companions of cerium*, and a few others."[17]

As a consequence, and in complete analogy with the alkali metals and the halogens, Mendeleev tried to accommodate the companions of cerium in the periodic table as a *group*. This fact is clearly exemplified in the *Attempted System* where the rare-earth elements (Er, Yt, Ce, La, and Di) are grouped together at the bottom of the system. Yet, Mendeleev promptly understood that the rare earths constituted a very *special* group of elements, and it seemed that the whole accommodation issue had its root in the puzzling nature of this *elementary group*. "A number of questions arise when all of the elements are arranged into one whole," Mendeleev said, "but the most interesting problem appears to me to be the *arrangement of elements having such similarity as* [. . .] *cerium*."[18]

11.1.5 Primary Versus Secondary Classification

In order to understand why Mendeleev discriminated this group from the other natural groups (such as the alkali metals and halogens), it will prove useful to explore the construction methodology of the periodic table. In short, a two-step process is needed in order to build a periodic table from scratch. First, all the elements have to be ordered according to increasing atomic weight. This *primary classification* results in a long horizontal sequence of elements, and has been called the *Mendeleev Line* by Henry Bent.[19] It will be noted that certain chemical and physical properties of the elements recur *periodically*. Therefore, the second step, termed *secondary classification*, consists of partitioning this Mendeleev Line at certain well defined loci and placing the different sections (i.e. *periods*) underneath each other so that elements with similar properties will fall into the same vertical column, forming *natural groups* and representing the periodic law graphically.

It seems that Mendeleev exploited this construction methodology as well—more in particular when he created his *first attempt*.[20] As Mendeleev explained:

[17] Ibid., p. 22. Emphasis added.

[18] Ibid., p. 31. Emphasis added.

[19] Bent, H. A. *New Ideas in Chemistry from Fresh Energy for the Periodic Law*. Bloomington, Indiana: AuthorHouse, 2006.

[20] The *first attempt* is not to be confused with the *Attempted System*. Whereas the *Attempted System* (Figs. 11.1 and 11.2) represents the end-product of the process of discovery, Mendeleev most probably wrote down the *first attempt* at the very beginning of his quest for a classification of the elements.

My first attempt in this direction was as follows: I selected the substances with the smallest atomic weights and arranged them according to the magnitude of their atomic weights [i.e. *primary classification*]. It became apparent that there existed, so to speak, a periodicity in the properties (even with regard to valency) of the simple substances [i.e. *periodic law*], when one element followed another according to a linear arithmetical arrangement of their atomic weights. [Secondary classification therefore led to]:

Li = 7	Be = 9.4	B = 11	C = 12	N = 14	O = 16	F = 19
Na = 23	Mg = 24	Al = 27.4	Si = 28	P = 31	S = 32	Cl = 35.5
K = 39	Ca = 40	_	Ti = 50	V = 51	_	_

In the division of elements with an atomic weight greater than 100 we encounter a completely analogous series:

Ag = 108	Cd = 112	Ur = 116	Sn = 118	Sb = 122	Te = 128	J = 127

It is seen that Li, Na, K, Ag show the same relationship to one another as do N, P, V, Sb, etc. [i.e. the formation of elementary groups as a result of *secondary classification*].[21]

11.1.6 Primary Versus Secondary Groups

One can conclude at this point that natural, elementary groups (e.g. Li, Na, K, . . ., Ag) are formed during the secondary classification. Within such a vertical group, the atomic weights of the congeners vary in a stepwise manner.[22] In the case of the alkali metals {Li, Na, K, . . ., Ag}, for example, one notices the following sequence of 'jumps' between the atomic weights: 7 ➠ 23 ➠ 39 ➠ . . . ➠ 108. We will denominate such a natural group of elements by the term *secondary group*, the members of which will be called *secondary elements*. Hence, a secondary group is defined and recognised as follows:

1. Secondary groups are formed during the secondary classification of the elements;
2. There exists a stepwise relationship between the atomic weights of the congeners.

Some examples of secondary groups are the alkali metals, the alkaline earth metals, the halogens, and the noble gases.

In sharp contrast with this type of natural groups, some other groups, such as the cerium group {Ce, La, Di}, are formed at an earlier stage of the construction methodology, namely during the *primary classification*. Worded somewhat differently, due to the fact that the elements constituting such groups succeed one another sequentially in the Mendeleev Line (e.g. Ce = 92, La = 94, Di = 95), the formation of these groups will be noticed during the primary classification. Within such a horizontal group, the atomic weight of the congeners will remain almost constant.

[21] Mendeleev (1869b/t), op. cit., p. 25. (see note 16)

[22] Congeners are elements in the same group of the periodic system.

Thus in the case of the elementary group {Ce, La, Di}, one observes the following sequence of atomic weights: 92 ➠ 94 ➠ 95. In what follows, such a natural group of elements will be denominated by the term *primary group* and their congeners by the name *primary elements*. Hence, primary groups are defined and recognised as follows:

1. Primary groups are formed during the primary classification of the elements;
2. There exists a steady, almost constant relationship between the atomic weights of the congeners.

Other examples of such primary groups are the iron group {Fe = 56, Ni = 59, Co = 59}, the platinum group {Pt = 197.1, Ir = 198, Os = 199}, the palladium group {Rh = 104.4, Rn = 104.4, Pl = 106.6},[23] and the erbium group {Er = 56, Yt = 60}.

In conclusion, and keeping the above-stated crucial distinction between primary and secondary groups in mind, it should be relatively easy at this point to understand the 'special' character of the rare-earth groups. That is to say, since the rare-earth elements constituted two primary groups, {Ce, La, Di} and {Er, Yt}, Mendeleev considered these groups 'special' as their congeners exhibited atomic weight values which were very close to one another, a fact not to be observed in the 'normal' case of secondary groups where the congeners have radically different atomic weights. In his article *On the Correlation between the Properties of the Elements and Their Atomic Weights*, Mendeleev wrote:

> A number of questions arise when all of the elements are arranged into one whole, but the most interesting problem appears to me to be the arrangement of elements having such similarity as iron, cerium, palladium, and platinum, since, in this case, *elements close to each other in their nature also exhibit approximately the same atomic weights*, a circumstance not to be observed in other rows, for in the latter *similar elements possess different atomic weights*.[24]

One can conclude that Mendeleev was blessed with a deep insight into the nature of and differences between elementary groups—a fundamental understanding, which in the eyes of the authors, is often lacking within the chemical community of the twenty-first century.

At least four important consequences can be drawn from the existence of primary groups: (1) the problematic depiction of both primary and secondary groups in the periodic table, (2) the transitional function of primary groups, (3) the rare earth—transition metal analogy, and (4) the problematic nature of primary groups, undermining the periodic law and subverting the characterisation of the elements by their atomic weight.

[23] In Mendeleev's nomenclature, Rn represented ruthenium and Pl represented palladium.

[24] Mendeleev (1869b/t), op. cit., p. 31. (see note 16) Emphasis added.

11.1.7 Table Layouts

First of all, Mendeleev naturally wondered how one should depict both primary and secondary groups within his *Attempted System*. "Perhaps as a consequence of the closer study of these [primary] groups," said Mendeleev, "the system of elements arranged in [primary and secondary] groups will have to be changed such that in certain parts of the system the similarity between members of the horizontal rows will have to be considered [i.e. secondary group], but in other parts, the similarity between members of the vertical columns [i.e. primary group]."[25] Notice that, in comparison with Mendeleev's *first attempt*, all rows and columns have been interchanged in the *Attempted System*. Thus what used to be a vertical group of elements in the *first attempt* (e.g. Li, Na, K, ...) has been transformed into a horizontal group in the *Attempted System*. As a result, all secondary groups are now lying horizontally. The primary groups, on the other hand, are laid out vertically in Mendeleev's *Attempted System*. Of course, whether a secondary group is lying horizontally (as in the *Attempted System*) or vertically (as in the *first attempt*) does not really matter. Of greater importance is the simultaneous existence of both primary *and* secondary groups in *one* classificatory system of the elements, and the way this is represented in the table layout.

11.1.8 Transitional Function of Primary Groups

A more significant consequence of the existence of primary groups within the periodic system is their so-called *transitional function*. Mendeleev hit upon this substantial idea when he was examining the *Attempted System*. It appeared to him that the elements of the primary groups at the upper part of his system represented some sort of transition between two (sub)periods in the periodic table. "It must be remarked," he said, "that the upper members of the fourth column (Mn, Fe, Co, Ni, Zn) form a *transition* to the lower members of the (third) column in which Ca, K, Cl and similar elements are found. Thus the properties and atomic weights of cobalt and nickel, chromium, manganese, and iron represent a *transition from copper and zinc to calcium and potassium*."[26] In all probability, this quotation lies at the origin of the term *transition metals*—a very powerful and important concept for the further development of the periodic table (see further). Nonetheless, at the beginning of 1869, Mendeleev's views on the matter were still rather intuitive and somewhat vague. Indeed, it was not easy to perceive the transitional function of the iron group, the palladium group, and the platinum group in the *Attempted System*.[27]

[25] Loc. cit.

[26] Ibid., p. 30. Emphasis added.

[27] The transitional function of these primary groups must have manifested itself much more sharply during the construction process of the *first attempt*.

11.1.9 The Rare Earth—Transition Metal Analogy

As a consequence of fixing all his attention on the *Attempted System*, Mendeleev immediately recognised how the two primary groups, {Ce, La, Di} and {Er, Yt}, at the bottom part of his system helped in connecting the periods of the main core. It thus seemed that these primary groups were furnished with a *transitional function* as well. Due to the fact that both the transition metal groups (iron, palladium and platinum group) and the rare-earth groups (cerium and erbium group) exhibited a transitional function, Mendeleev quickly emphasised the similarity between these two sets of groups. Mendeleev first voiced these ideas in his 1869 article *On the Correlation between the Properties of the Elements and Their Atomic Weights*, where he wrote:

> Perhaps for this reason [the] positions [of the iron group, the palladium group, and the platinum group] will have to be changed and, were they to be placed in the lower rows instead of the upper rows, then one would obtain three columns here which would, in many respects, exhibit *similarities*: one column containing cobalt, nickel, chromium, manganese, and iron [as well as Er, Yt, and In]; a second column containing cerium, lanthanum, and didymium, palladium, rhodium, ruthenium, and lastly, a third columns containing platinum, iridium, and osmium.[28]

The rare earth—transition metal analogy was further exemplified by Mendeleev in his article *Concerning the Atomic Volumes of Simple Bodies* (presented on 23 August 1869). Referring to the work of Wiedemann, Mendeleev emphasised the similarity in magnetic properties between the elements of the cerium group and of the iron group. Not only were all these elements "magnetic in their compounds", "their atomic magnetism [remained] similar when passing from one analogue to another."[29] Repeated references to the rare earth—transition metal analogy were also made in his article *On the Quantity of Oxygen in Metal Oxides and on the Valency of the Elements* (presented on 2 October 1869) and in the second volume of his *Osnovy khimii*, published in March 1870.

11.1.10 Undermined Periodicity

A fourth and last consequence of the existence of primary groups was their problematic nature—undermining both the periodic law and the characterisation of elements as being defined by their atomic weight. Let us start with the subversion of periodicity. Mendeleev explained that "the arrangement of elements [...] according to the magnitude of their atomic weights corresponds to their so-called valencies and, to a certain degree, to the differences in their chemical

[28] Mendeleev (1869b/t), op. cit., p. 30. (see note 16) Emphasis added.

[29] Mendeleev, D. I. "Concerning the Atomic Volumes of Simple Bodies." In *Arb. IIKongr. Russ. Arzt. Naturf.*, 1869e. English translation by Trifonov, D. N. "Mendeleev and the Rare Earths." In *Problems in the Study of Rare Earths*, 28. Jerusalem: Israel Program for Scientific Translations, 1966.

characters".[30] According to Mendeleev, this "can be clearly seen in the row Li, Be, B, C, N, O, F"[31]:

	Li = 7	Be = 9.4	B = 11	C = 12	N = 14	O = 16	F = 19
Valency	1	2	3	4	3	2	1

Thus, "Li and F are monovalent and are most widely separated with respect to electrochemical behaviour; Be and O, which succeed them, are divalent; then come trivalent B and N and, in the centre, tetravalent carbon has its place."[32] This phenomenon appeared moreover to be "repeated in other rows".[33] "If we consider the distance between Na and Cl, Ag and I, and others," Mendeleev remarked, "we also notice that the arrangement of elements according to the magnitude (of their atomic weights) corresponds in a certain degree to the valency and to the concept of affinity."[34] Due to the recurring nature of this phenomenon, Mendeleev concluded that, "when arranged according to their atomic weights, the elements display a distinct periodicity in their properties".[35] Mendeleev's personal viewpoints on the *periodic law* were even more clearly stated in the first edition of his *Osnovy khimii*:

> The regular and gradual *changes in the size of atomic weights involves* [. . .] *the regular and gradual changes* in the qualitative as well as in the quantitative *capability of elements for compounds*. In addition, there is a *periodic repetition* of both qualitative and quantitative characteristics, consonant with the gradual increase in atomic weight. This is the conclusion of all comparisons made in this regard and this opens, in my view, a new perspective on the elements.[36]

Mendeleev's insight in the subject matter, as well as the vital importance of the *periodic law* in classifying the chemical elements, cannot be overestimated. Nevertheless, and quite unfortunately, it could not be accredited a universal character, as it did not apply to the whole of chemical elements. After all, in the case of primary groups, there were of course "regular and gradual changes in the size of atomic weights",[37] *but* these were *not* accompanied by "the regular and gradual changes"[38] in the distinctive properties of the elements. In the case of the cerium group, for example:

	Ce = 92	La = 94	Di = 95
Valency	2	2	2

[30] Mendeleev (1869b/t), op. cit., p. 33. (see note 16)

[31] Loc. cit.

[32] Ibid., p. 27.

[33] Ibid., p. 33.

[34] Ibid., p. 27.

[35] Ibid., p. 33.

[36] Mendeleev, D. I. *Osnovy Khimii*. 2 vols. 1st ed. St. Petersburg: Obshchestvennaia pol za, 1868–1871. English translation by Trifonov, D. N. "Views of D. I. Mendeleev on Rare Earths." In *Rare-Earth Elements and Their Position in the Periodic System*. New Delhi: Indian National Scientific Documentation Centre, 1970. Emphasis in original.

[37] Loc. cit.

[38] Loc. cit.

there appears to be a constancy in the valency number, although the atomic weights of the congeners are changing regularly and gradually. The same can be said for the iron group, the palladium group, the platinum group, and the erbium group. In conclusion, the generality of the periodic law got undermined due to the presence of primary groups in the periodic system. This was one of the core problems of the rare-earth elements, which lay at the basis of their problematic accommodation.

11.1.11 Characterisation Issues: Primary Versus Secondary Elements

The dual sense of the epistemological concept of chemical elements has been the focus of much philosophical debate and research by contemporary philosophers of chemistry. Although this debate goes back to the 1931 paper by Paneth,[39] the main idea was clearly already present in the Mendeleev corpus.[40] It is therefore interesting to investigate to what extent the rare-earth crisis forced Mendeleev to change his points of view with regard to the nature and concept of elements.

Summarising Mendeleev's philosophical viewpoints, one could state that Mendeleev clearly recognised the dual sense of the nature of chemical elements. He thus clearly distinguished between the elements as *simple substances* and as *basic substances*. Simple substances could be characterised by the plethora of secondary properties (i.e. colour, taste, smell, etc.), and were therefore observable and isolable. Basic substances on the other hand were completely unobservable to our senses. This did not imply however that they were completely devoid of properties. Mendeleev was of the opinion that the more abstract, basic substances were characterised by the atomic weight, and he therefore used this property in

[39] Paneth, F. A. "Über Die Erkenntnistheoretische Stellung Des Chemischen Elementbegriffs." *Schriften der Königsberger Gelehrten Gesellschaft* 8, no. 4 (1931): 101–125. An English translation can be found in Paneth, F. A. "The Epistemological Status of the Chemical Concept of Element (I)." *The British Journal for the Philosophy of Science* 13, no. 49 (1962a): 1–14 and Paneth, F. A. "The Epistemological Status of the Chemical Concept of Element (II)." *The British Journal for the Philosophy of Science* 13, no. 49 (1962b): 144–160. More recently, Paneth's paper has been republished in Paneth, F. A. "The Epistemological Status of the Chemical Concept of Element." *Foundations of Chemistry* 5, no. 2 (2003): 113–145.

[40] See Paneth, F. A. "Chemical Elements and Primordial Matter: Mendeleeff's View and the Present Position." In *Chemistry and Beyond*: *Selection from the Writings of the Late Professor F.A. Paneth*, edited by Herbert Dingle and G. R. Martin, 53–72. New York: Wiley Interscience, 1965. See also Bensaude-Vincent, B. "Mendeleev's Periodic System of Chemical Elements." *The British Journal for the History of Science* 19, no. 1 (1986): 3–17, Scerri, E. R. "Realism, Reduction, and the "Intermediate Position"." In *Of Minds and Molecules*, *New Philosophical Perspectives on Chemistry*, edited by N. Bhushan and S. Rosenfeld, 51–72. New York: Oxford University Press, 2000, Scerri, E. R. "Some Aspects of the Metaphysics of Chemistry and the Nature of the Elements." HYLE 11, no. 1–2 (2005): 127–145.

accommodating all the chemical elements in his system. "In the proposed system the *atomic weight* of an element serves to *determine its* place",[41] Mendeleev explained. He concluded for that reason that "the magnitude of the *atomic weight determines the character of an element* to the same extent that the molecular weight determines the properties and many of the reactions of a compound substance."[42] An important consequence of taking the atomic weight as the characteristic property of basic substances was the possibility of distinguishing between the (chemically and physically very similar) congeners of a certain elementary group in the periodic table. The natural group of alkali metals, for example:

Li = 7	Na = 23	K = 39	Rb = 85.4	Cs = 133

consisted of five metals which shared a lot of similar properties—their metallic lustre, their low melting points and densities, their pronounced reactivity with respect to water, their rapidly oxidising character (tarnishing the metallic surface in a dull and lustreless grey colour), etc. It thus seemed that the differences in atomic weights were the only possible way to differentiate between these analogous elements. "Similar elements [in chemical and physical properties] possess different atomic weights",[43] Mendeleev proclaimed.

But in the case of the cerium group {Ce = 92, La = 94, Di = 95}, the difference in atomic weights was scarcely noticeable. Indeed, one recalls that in sharp contrast with the *secondary groups*, which were characterised by a saltatory relationship between the atomic weights of the *secondary elements*, *primary groups* represented a steady and unchanging relationship between the atomic weights of the *primary elements*. As Mendeleev explicated in his *Osnovy khimii*: "In spite of the great similarity existing at present [between the chemical and physical properties of the congeners of the cerium group], there are no differences, or to speak precisely, there are *no considerable differences in the values of atomic weights* of [these] similar elements."[44] "There are more examples of this kind",[45] wrote Mendeleev, who noticed that this observation was not limited to the members of the cerium group. It turned out that very similar apperceptions could be made with regard to the transition metal groups:

> Such are nickel and cobalt, whose *atomic weights are very close to each other*; rhodium, ruthenium and palladium on the one hand, iridium, osmium and platinum on the other are also elements which closely resemble one another, and which have *very similar atomic weights*. Iron and manganese have similar properties and their *atomic weights are also very similar*.[46]

[41] Mendeleev (1869b/t), op. cit., p. 26. Emphasis added. (see note 16)

[42] Ibid., p. 27. Emphasis added.

[43] Ibid., p. 31.

[44] Mendeleev (1868–1871), op. cit. (note 36) English translation by Trifonov (1970), op. cit., p. 38. (note 36) Emphasis added.

[45] Loc. cit. English translation by Trifonov (1966), op. cit., p. 27. (note 29)

[46] Loc. cit. Emphasis added.

This implied that, in the case of primary groups, no differentiation between the congeners was possible anymore on the basis of their atomic weights. Otherwise stated, while *secondary elements* could still be characterised by their atomic weights, *primary elements*, on the other hand, *could no longer be characterised by the atomic weight*!

11.1.12 Internal Differences of Matter

The question naturally presented itself as to how one should differentiate between primary elements. According to Mendeleev, these elements were characterised by "*internal differences of matter*".[47] The reason for the differences "is no longer the size and the weight of the atom," he said, "but obviously some other *internal differences in the matter*, constituting the atoms of these similar elements".[48] This was comparable in some respects with *isomeric substances*, as well as with *metameric compounds*, which were defined by Mendeleev as having "the same weight of particle [i.e. molecular weight] but in which the distribution of parts or atoms inside the particle is undoubtedly not identical".[49] While Mendeleev clearly stated that "elements of a similar nature, with similar atomic weights [i.e. primary elements], are somewhat similar to metameric compounds",[50] it is not completely clear whether he actually believed in the *complexity of atoms*. After all, whereas Mendeleev referred to the "internal differences in the matter, *constituting the atoms*", Mendeleev also mentioned the "internal *arrangement of atoms*" at a certain point. Did he mean that the atoms were different due to an internal arrangement (thus believing in the complexity of atoms), or was he alluding to an internal difference in the arrangement of atoms inside a molecule? In any case, whether Mendeleev believed in the complexity of atoms or not, he definitely believed in the existence of atoms during the period 1869–1870. At that time, Mendeleev was giving his thoughts about the periodic system free rein. He was still prepared to accept the atomic hypothesis and he believed in both the chemical and physical atom.

In sharp contrast with the above-mentioned statement, the famous Mendeleev historian, Michael Gordin, claimed in his book on *Dmitrii Mendeleev and the Shadow of the Periodic Table* that "it does not follow [...] that Mendeleev must have been thinking in terms of physical atomism when he conceived his system. [...] Mendeleev's scepticism toward atomism sharply emphasises the difference between the present-day interpretation of the periodic system and Mendeleev's views of 1869. [...] For Mendeleev, any atoms that might exist had *absolutely no*

[47] Loc. cit. English translation by Trifonov (1970), op. cit., p. 38. (note 36) Emphasis added.
[48] Loc. cit. English translation by Trifonov (1966), op. cit., p. 28. (note 29)
[49] Loc. cit.
[50] Loc. cit.

substructure."[51] Bernadette Bensaude-Vincent as well, claimed that the elements "could never be divided" according to Mendeleev's opinion.[52] Finally, the Japanese historian, Masanori Kaji asserted that "Mendeleev regarded atomic theory with caution" and Kaji therefore thought it reasonable "to suppose that [Mendeleev] refined the concept of the elements to bear an attribute of an individual chemical entity *without* employing the notion of atoms because of the supposed limitations of the atomic theory."[53]

How to explain this difference in opinion? As we have argued elsewhere,[54] Mendeleev *did* believe in atoms in 1869. But these viewpoints no longer surfaced in the papers which were written at a later stage of development of the periodic law (i.e. during the post-1869 period). At that time, Mendeleev had indeed radically changed his viewpoints concerning the existence of atoms. He thus emphasised in 1871 that "one cannot harmonise the periodic law and the atomic theory without upsetting the known facts."[55] Since the expression atomic weight implied "the hypothesis of the atomic structure of matter", Dmitrii Ivanovich proposed to replace this expression with "elementary weight" as it seemed to him that this would "avoid the concept of atoms when speaking of elements."[56] Such statements from the post-1869 period have led the majority of historians to the wrong conclusion that Mendeleev *never* believed in atoms. It appears that Nathan Brooks has been one of the few historians thus far in emphasising Mendeleev's speculations on the complexity of the elements in 1869. He thus clearly stated that "Mendeleev did *not* reject the complexity of elements in the first few years after his discovery of the periodic law."[57]

Thus ended the first period of Mendeleev's research which lasted from 1869 till the end of the first half of 1870. Mendeleev's viewpoints could be summarised as follows. According to his opinion, chemists had to draw a sharp distinction between *primary* (i.e. rare earths, transition metals) and *secondary* elements (i.e. alkali metals, halogens). Such a differentiation should also be made on the

[51] Gordin, M. D. *A Well–Ordered Thing*: *Dmitrii Mendeleev and the Shadow of the Periodic Table*. New York: Basic Books, A Member of the Perseus Books Group, 2004. (pages 24–25) Emphasis in original.

[52] Bensaude-Vincent, B., op. cit. p. 7. (note 40)

[53] Kaji, M. "D. I. Mendeleev's Concept of Chemical Elements and the Principles of Chemistry." *Bulletin for the History of Chemistry* 27, no. 1 (2002): 4–16. (page 6–7) Emphasis added.

[54] Thyssen, P. "Mendeleev's Periodic Table and the 19th Century Debates on Atomism." In *Wald*, *Positivism and Chemistry*. Edited by M. Eisvogel and K. Ruthenberg. Würzburg: Konigshausen and Neumann, 2014 (in press).

[55] Mendeleev, D. I. "Die Periodischen Gesetzmässigkeit Der Chemischen Elemente." *Annalen der Chemie und Pharmacie* 8 (Suppl.) (1871c): 133–229. English translation in Mendeleev, D. I. "On the Periodic Regularity of the Chemical Elements." (1871c/t) In *Mendeleev on the Periodic Law*, *Selected Writings*, *1869–1905*, ed. William B. Jensen, 38–109. Mineola, New York: Dover Publications, Inc., 2002. (page 58)

[56] Ibid., p. 40 & 106.

[57] Brooks (2002), op. cit., p. 142. (note 10)

level of *primary* and *secondary* groups. Mendeleev thus concluded his paper of 1869 by noting that while all elementary groups were build from "elements exhibiting similarities in their chemical behaviour" differences in their nature would continue to exist, since the atomic weights of their congeners "are either approximately equal (as with Pt, Ir, Os) or [...] increase in a uniform manner (as with K, Rb, Cs)."[58]

The essence of the rare-earth crisis rested on the fact that the septuplet of homeless elements constituted a primary group. Their problematic nature raised a number of serious problems. Both the principle of periodicity and the characterisation of primary elements on the basis of their atomic weights got undermined. Mendeleev was also tempted in drawing an analogy between the rare-earth elements and the transition metals on the basis of their transitional functions in the periodic system, and he started questioning the simplicity of these elements on a closer study of the primary groups. In conclusion, Mendeleev clearly grasped the causes of the problematic accommodation of the rare-earth elements in 1869. He nevertheless continued to use the old atomic weights and erroneous valencies for the rare-earth elements, and his unremitting adherence to the *Attempted System* moreover troubled his views with regard to the different relationships between the chemical and physical properties of the elements.

11.2 The Period 1870–1871

11.2.1 Natural System of the Elements

Mendeleev had been working on the optimisation of the periodic law for quite some time now. He had always preferred the *long form* table (i.e. *Attempted System*, Figs. 11.1 and 11.2), but in November 1870, Mendeleev created a *short form* table—his *Natural System of the Elements* (Fig. 11.4). This type of classification remained the standard format during the next 100 years, and it succeeded in exhibiting a number of new relationships between the chemical elements (as for example the close connection between the main-block elements on the one hand and the transition metals on the other).

The *Natural System* consisted of two rows of *typical elements* (H till F) and five more *periods* which were further subdivided in an odd and even *series* of seven elements each. Some elements could not be placed in any series and were therefore "arranged in order of their properties and atomic weights between the last member of the even series and the first member of the odd series" in an independent, eighth group.[59] "In this manner", Mendeleev continued, "Fe, Co, and Ni are placed

[58] Mendeleev (1869b/t), op. cit., p. 33. (note 16)

[59] Mendeleev (1871c/t), op. cit., p. 48. (note 55). See also Sect. 11.1, five for an illustration of the construction methodology when building a short form table (i.e. *first attempt*).

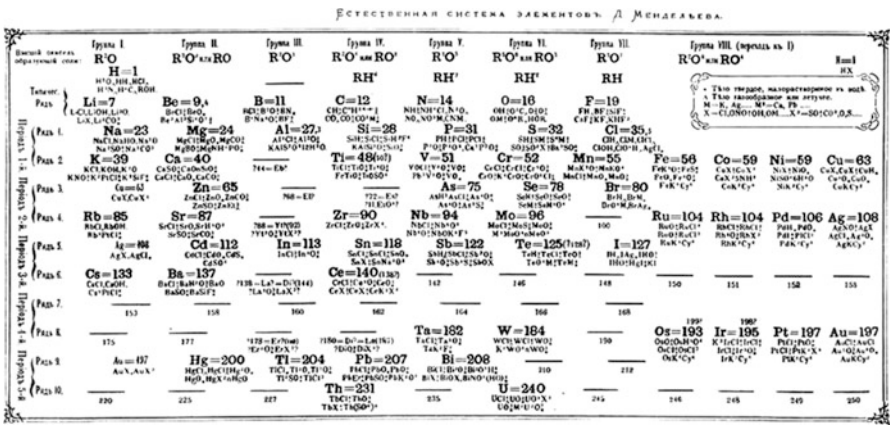

Fig. 11.4 Mendeleev's *Natural System* of the elements from 1870

between Cr and Mn, on the one side, and Cu and Zn, on the other, so as to form the following *transition series*:"[60]

Cr = 52	Mn = 55	Fe = 56	Co = 59	Ni = 59	Cu = 63	Zn = 65

Two other triads of transition metals could be discerned in the *Natural System*: the elements Ru, Rh and Pd, on the one hand, and Os, Ir and Pt on the other (Fig. 11.4).

Mendeleev emphasised that "the members of this group [. . .] resemble one another to the same extent as the corresponding members of the even series",[61] with the only difference that they constituted three *primary groups*, instead of *secondary groups* as in the case of the elements from the groups I–VII. Notice also that these groups were *horizontally* orientated, just as Mendeleev had predicted back in 1869, when he said that perhaps the system of elements would have to be changed "such that in certain parts of the system the similarity between members of the horizontal rows [i.e. primary elements] will have to be considered, but in other parts, the similarity between members of the vertical columns [i.e. secondary elements]."[62]

One can conclude that Mendeleev was aided significantly by his construction of the short form table in defining the transition metals more clearly than before as those elements which connected the even and odd series.

[60] Loc. cit. Emphasis added.

[61] Loc. cit.

[62] Mendeleev (1869b/t), op. cit., p. 31. (note 16)

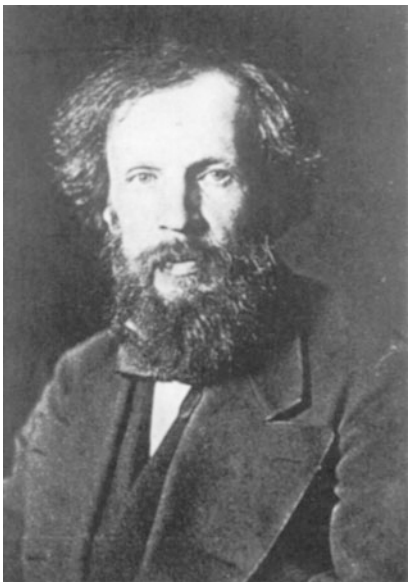

Fig. 11.5 Dmitrii Ivanovich Mendeleev in the year 1870

11.2.2 Atomic Weight Corrections and Valency Shifts

In that same year 1870, Mendeleev (Fig. 11.5) also wrote an article *On the Placement of Cerium in the Periodic System of Elements*, where he admitted that "the atomic weights of indium, uranium and cerium (and probably its associates) should be modified because these elements do not fit in on the basis of either the form of their oxides or their properties according to the periodicity indicated by me."[63] He realised that a change in valency would be necessary in order to correct the atomic weight values of the rare earths. The usual representation of their oxides by the formula RO had thus to be modified. Mendeleev was the first in assuming the rare earths to be trivalent, instead of bivalent, and he therefore proposed the general formula R_2O_3 for the rare-earth oxides. In the case of cerium, which represented two degrees of oxidation, Mendeleev proposed "that the ordinary degree of oxidation [...] be allotted the formula Ce_2O_3", while "the higher oxide will have the simple composition CeO_2."[64] Similar statements appeared in his article *Concerning the Natural System of the Elements and Its Application in Determining the*

[63] Mendeleev, D. I. "On the Placement of Cerium in the Periodic System of Elements." *Bulletin de l'Academie imperiale des sciences de St.–Pétersbourg* 16 (1870/1871): 45. English translation by Trifonov (1970), op. cit., p. 40. (note 36) This paper was completed in November 24, 1870. Originally, Mendeleev had written one big article on "the system of the elements" but this was afterwards subdivided in Mendeleev (1870/1871) and Mendeleev (1871a). (note 65)

[64] Loc. cit. English translation by Trifonov (1966), op. cit., p. 25. (note 29)

Properties of Undiscovered Elements.[65] These valency shifts implied that the currently used atomic weights would have to be increased by a factor of 1.5.

As Mendeleev wrote in his article *On the Placement of Cerium in the Periodic System of Elements*: "To confirm the above ideas, I undertook the problem of determining the heat capacity of the above-mentioned metals."[66] The experimental results, obtained in the fall of 1870, were confirmed by the investigations of Bunsen and spoke in the advantage of the corrected atomic weights.

11.2.3 Accommodating the Rare Earths Individually

When the atomic weight of an element is changed, this logically implies a change in its position in the periodic table. Thus, due to the atomic weight corrections of indium, uranium, cerium, lanthanum, didymium, yttrium, erbium, and thorium, all eight elements had to be removed from their usual place, and they had to be accommodated differently. As can be seen from Fig. 11.4, Mendeleev placed the rare-earth elements throughout the sixth, seventh, and eighth subperiods of his system in the groups I–VIII, as *homologues* of the other elements, according to a *homologous accommodation methodology*.

The accommodation of cerium went smoothly as Mendeleev had correctly determined its atomic weight and oxide formulae. According to the dualism of cerium, this rare-earth element exhibited two oxidation states (+III and +IV), making its placement in the fourth group very natural. As Mendeleev reasoned in his article *On the Placement of Cerium in the Periodic System of Elements*:

> Cerium will [have to] be located in accordance with the value of its atomic weight following caesium 133 and barium 137, and in accordance with the formula of its higher degree of oxidation it should be located in the titanium group, i.e., in the place IV–6.[67]

The placement of lanthanum, didymium and the other rare earths proved much more difficult. Mendeleev finally decided to locate yttrium in the place III–4. Lanthanum seemed to fit in the place III–6 and didymium was finally given the

[65] Mendeleev, D. I. "Concerning the Natural System of the Elements and Its Application in Determining the Properties of Undiscovered Elements." *Zhurnal Russkogo Khimicheskogo Obshchestva* 3 (1871a): 7, 25–56. See also a German abstract in Mendeleev, D. I. "Über Das Natürliche System Der Elemente Und Seine Anwendung Zum Ermitteln Der Eigenschaften Unentdeckter Elemente." *Berichte der Deutschen chemischen Gesellschaft* 3 (1870b): 990–992.

[66] Mendeleev (1870/1871), op. cit. (note 61) English translation by Trifonov (1970), op. cit., p. 40. (note 36)

[67] Loc. cit. English translation by Trifonov (1966), op. cit., p. 25. (note 29) Due to the table layout—consisting of eighth groups (I–VIII) and ten series (1–10)—each element (*X*) can be characterised by two coordinates, its group number (*G*) and its series number (*S*), as *G*–*S*. Sodium for example, is located in the first group and first series, and is therefore given the element coordinates I–1. Magnesium is located in the place II–1, and titanium is characterised by the element coordinates IV–2.

Reihen	Gruppe I. $\frac{}{R^2O}$	Gruppe II. $\frac{}{RO}$	Gruppe III. $\frac{}{R^2O^3}$	Gruppe IV. $\frac{RH^4}{RO^2}$	Gruppe V. $\frac{RH^3}{R^2O^5}$	Gruppe VI. $\frac{RH^2}{RO^3}$	Gruppe VII. $\frac{RH}{R^2O^7}$	Gruppe VIII. $\frac{}{RO^4}$
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199
11	(An=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

Fig. 11.6 Mendeleev's Natural System of the elements in 1871

element coordinates V–6, although Mendeleev was still playing with the idea of placing didymium in the same spot as lanthanum in III–6, as can be seen from Fig. 11.4.

This homologous placement of the rare-earth elements shows to what extend Mendeleev's viewpoints had changed by the end of the first half of 1870. What catches the eye is that Dmitrii Ivanovich had switched from placing the rare-earth elements as a *group* in the periodic system to an *individual* placement of each element separately (Fig. 11.6). That is, by breaking up the natural group of rare earths, Mendeleev ended up with a set of distinct elements which he set out to accommodate on an individual basis in *different* groups of the system.

While this individual accommodation of the rare-earth elements represented an interesting step forward, it did not remove all problems. Mendeleev had always used "a web of analogies" in determining the positions of the chemical elements, but this methodology could no longer be applied in the case of the rare earths. As Nathan Brooks observed, "the rare-earth elements exposed a serious weakness in Mendeleev's approach to solving the placement of elements in his periodic system."[68] Not surprisingly, Mendeleev remained doubtful as to the new positions of the rare-earth elements.

Yet, the homologous placement offered a number of advantages as well. By emphasising the *individuality* of the rare earths, Mendeleev denied the existence of a *primary group* of rare-earth elements, which implied he could set aside all problems connected with the existence of such primary groups—in particular, the danger of undermined periodicity and the seeming impossibility of characterising the elements, as basic substances, by their atomic weights.

[68] Brooks (2002), op. cit., pp. 138–139. (note 10)

11.2.4 Saving the Periodic Law

Let us try to explain this last point somewhat better. One recalls that the periodic law got undermined by the existence of primary groups due to the fact that the "regular and gradual changes in the size of atomic weights" were not accompanied by "the regular and gradual changes" in the distinctive properties of the elements.[69] Thus, in the case of the cerium group:

	Ce = 92	La = 94	Di = 95
Valency	2	2	2

the valency number (i.e. oxidation state) remained constant, instead of gradually increasing. If, however, these elements were accommodated as *homologues* of the third, fourth and fifth group respectively, their valency also gradually increased from 3 to 4 and 5, thus resolving the problem entirely:

	La = 138	Ce = 140	Di = 144
Valency	3	4	5

Mendeleev was swift at drawing an important conclusion from this: the typically trivalent rare-earth elements had to exhibit some higher oxidation states as well. Cerium, for example, was located in the fourth group with the *tetravalent* transition metals titanium and zirconium, while didymium was taken to be a homologue of the *pentavalent* metals vanadium and niobium. Neither the tetravalency of cerium nor the pentavalency of didymium had as yet been established however, and Mendeleev therefore planned to start his own rare-earth research, in the hope of revealing these higher oxidation states. This would prove the validity of the homologous accommodation methodology and would rescue the periodic law from a painful exception.

11.2.5 Resolving the Characterisation Issues

Previously, the differences in atomic weight values between lanthanum, cerium and didymium had been too small to differentiate between these three elements. This undermined Mendeleev's use of the atomic weight as the characteristic property of basis substances, and led Mendeleev to believing in physically real atoms and an internal matter constituting these atoms.

The individuation of the rare-earth elements in the second period turned these elements from primary into secondary elements. Since the transition metals

[69] Mendeleev (1868–1871), op. cit. (note 36) English translation by Trifonov (1970), op. cit., p. 38. (note 36) Emphasis added.

continued to be primary elements, Mendeleev withdrew his claims about the rare earth—transition metal analogy. More importantly, by destroying the primary group of rare-earth elements, and accommodating them on an individual basis, Mendeleev created three new secondary groups, where the differences in atomic weight between lanthanum, boron and yttrium, for example, were big enough to use them as a characteristic, differentiating property. This removed the need to speculate about the existence of atoms, or the complexity of the elements.

11.2.6 Mendeleev's Active Rare-Earth Research

The improved format of Mendeleev's table had revealed a number of interesting relationships between the properties of the elements. Encouraged by this new information, Dmitrii Ivanovich began to focus all his attention on predicting the properties of the as yet undiscovered elements (i.e. eka-boron in III–2, eka-aluminium in III–3, and eka-silicon in IV–3, Fig. 11.4). He finished writing his paper *Concerning the Natural System of the Elements and Its Application in Determining the Properties of Undiscovered Elements* on the 29th of November 1870 and he presented his work during a meeting of the *Russian Chemical Society* in early December 1870.

With the predicted properties at hand, Mendeleev soon embarked upon his quest for the unknown elements. The position of eka-silicon (IV–3) implied that its properties would lie midway between those of titanium and zirconium, and Mendeleev therefore thought it best to initiate his hunt for this element in the minerals of titanium and zirconium. Two days after the meeting of the *Russian Chemical Society*, on the 5th of December 1870 to be exact, Mendeleev sent a petition to the rector of the University of St. Petersburg, K. F. Kessler, requesting him a number of minerals for his future investigations. "My observation of the periodic dependence between the properties and the atomic weights of simple bodies gives the possibility to predict the existence and to guess the properties of some simple bodies that have not yet been discovered, about which I communicated at an extraordinary session of the *Russian Chemical Society*", said Mendeleev.[70] "Desiring to verify at least part of the conclusions expressed [at this meeting], I need to undertake investigations of several rare minerals, and therefore request that you contact the Mining Institute to ask them for some of these minerals needed for my scientific work which they have in stock."[71]

Mendeleev continued how especially important it was for him "to obtain as large an amount of titanium minerals as possible, together with their place of origin, if possible. Specifically: rutile [TiO_2], ilmenite [$FeTiO_3$], and also other minerals: zirconium [Zr], orthite, or cerite and eschynite."[72] Dmitrii Ivanovich quickly

[70] Brooks (2002), op. cit., p. 138. (note 10)

[71] Loc. cit.

[72] Loc. cit.

obtained the requested minerals from P. A. Kochubei and he read in the accompanying letter: "I am sending you according to your request the following minerals: (1) eschynite, (2) ilmenite, and (3) perovskite. The first and last minerals I have managed to obtain from stock with great difficulty—and this took place not without damage to the best specimens, but I will not complain if the results you will obtain justify your expectations."[73]

The reason why Mendeleev asked for some specimens of rutile, ilmenite and zirconium should be clear by now. But why was he in need of orthite, cerite, and eschynite? Both cerite and eschynite are rich in cerium (and to a lesser degree also in lanthanum and yttrium). The mineral orthite, on the other hand, is not only abundant in cerium, it also contains substantial amounts of the other rare-earth elements. Obviously, Mendeleev was not only planning to discover the unknown eka-silicon, he also hoped to perform some experimental research on the rare earths in order to resolve their problematic accommodation.

As soon as he had received his mineral supplies from the Mining Institute and the Russian Technical Society, Dmitrii Ivanovich enthusiastically embarked upon his quest for eka-silicon and he also initiated his investigations of the rare-earth elements—trying to prove the validity of his *homologous accommodation methodology*. As Gordin stated, "he even refused a post at Moscow University on the grounds that he did not want to give up his current research on the rare earths."[74] Mendeleev pasted two periodic tables in his laboratory notebooks and he used them as a newfangled and powerful paper tool to guide his modern chemical research (Fig. 11.7).[75] As can be seen from the figure, Mendeleev had scribbled some of the rare-earth elements in thick red characters in the third group of his natural system.

According to Nathan Brooks, "Mendeleev spent considerable time trying to separate the four known rare-earth elements over the course of about one year, but he only met with failure. The difficulty was compounded because two of these rare earths (didym and erbium) later turned out to be mixtures of several elements and not pure elements."[76] As a consequence "Mendeleev's patience with this research agenda ran out quickly".[77] On the twentieth of December 1871, after scribbling no more than 67 pages in his lab book, Mendeleev decided to abandon all research on the rare-earth metals, and he set off on a gas project in search of the luminiferous ether. "On this date, on this page," said Gordin, "we can pinpoint the death of *all* research by Mendeleev on the periodic system. Gas expansion, not elemental discovery, became his goal."[78] At the upper left hand corner of his short form system, above hydrogen, Dmitrii Ivanovich had scrawled: "The ether is lighter than all of them by a million times" (Fig. 11.7).[79]

[73] Loc. cit.

[74] Gordin (2004), op. cit., p. 43. (note 51)

[75] Loc. cit.

[76] Brooks (2002), op. cit., p. 138. (note 10)

[77] Gordin (2004), op. cit, p. 50. (note 51)

[78] Loc. cit.

[79] Ibid., p. 52.

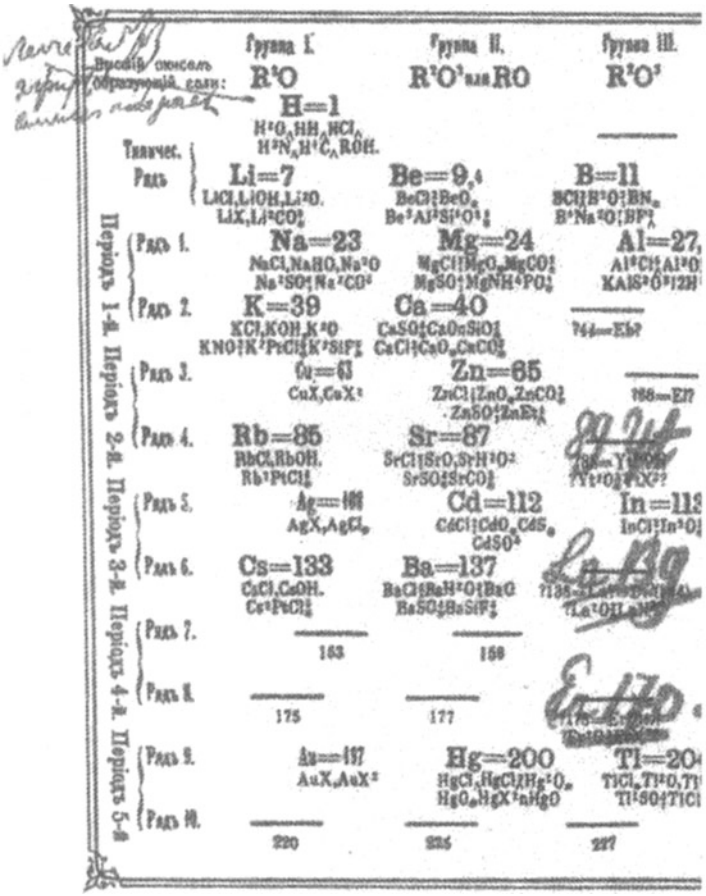

Fig. 11.7 Periodic system from Mendeleev's laboratory notebook on gas expansion (Source: Gordin (2004), op. cit., p. 53 (note 51). Original source: Mendeleev, Nauchnyi arkhiv: Periodicheskii zakon, photocopy 29)

Thus ended Mendeleev's experimental research on the periodic law as well as his rare-earth investigations. In July 1871, Mendeleev composed his German landmark article on the periodic law, which was translated into German by Felix Wreden and which appeared in *Liebig's Annalen* in November 1871—symbolising Mendeleev's last research paper on the periodic law.[80]

From all the papers Mendeleev had written in the period 1869–1871, this paper proved most valuable for the next generation of chemists who were on the verge of embarking on their own rare-earth studies. A definite proof as to the validity of the homologous accommodation methodology was still lacking. "It is here",

[80] Mendeleev (1871c/t), op. cit. (note 55)

Mendeleev said, "more than elsewhere in the system of elements, that new investigations are to be desired and for which the periodic law provides guidance."[81]

About 6 years later, the young Czechoslovakian chemist, Bohuslav Brauner, discovered Mendeleev's "wonderful communication". It made such a profound impression on him that he fixed his life's aim at that very moment: "it was the experimental research of the solution of the following problems: What is the position of the so called rare elements and especially those of the rare earths in Mendeleev's system?"[82] Brauner would become the main defender of the periodic system in the late nineteenth century, and his rare-earth research became of the utmost importance for the further resolution of the rare-earth crisis. But that is another story.[83]

11.3 Conclusions

Dmitrii Ivanovich Mendeleev definitely grasped the essence of the rare-earth crisis better than anyone else. His train of thought had been meticulously written down in a number of papers on the periodic law during the period 1869–1871. But Mendeleev not only circumscribed the rare-earth problem, he also significantly aided in partly resolving the crisis. Thus Mendeleev corrected the atomic weight values of the rare-earth elements by increasing their valency from 2 to 3, and he attempted to accommodate these metals on an individual basis according to a homologous placement. From the very beginning in 1869, Mendeleev had a sound conception of the difference between primary and secondary groups of elements. He discerned basic substances from simple substances, and he knew the advantages and disadvantages of both the short and long form tables.

Since Mendeleev's viewpoints underwent some crucial changes around the second half of 1870, this paper was divided in two main parts. The first period was characterised by Mendeleev's use of a *long form* periodic table (the *Attempted System*, Figs. 11.1 and 11.2) and his attempt to accommodate the rare-earth elements as a *group*. The rare earths thus constituted a primary group of primary elements, undermining both the periodic law and the characterisation of basic substances by their atomic weights. The old, Berzelian atomic weights were used throughout and Dmitrii Ivanovich endeavoured to grasp the rare-earth crisis by drawing an analogy between these elements and the so-called transition metals.

[81] Mendeleev (1871c/t), op. cit., p. 81. (note 55)

[82] Brauner, B. "D. I. Mendeleev as Reflected in His Friendship to Professor Bohuslav Brauner." *Collection of Czechoslovak Chemical Communications* 2 (1930): 219–243 (page 231).

[83] Thyssen, P., and K. Binnemans. "Accommodation of the Rare Earths in the Periodic Table: A Historical Analysis." In *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, 41, 1–94. Burlington: Academic Press, 2010.

In sharp contrast with the first period, the second period was characterised by Mendeleev's use of a *short form* periodic table (the *Natural System*, Figs. 11.4 and 11.6). He aimed at an *individual* accommodation of the rare-earth elements, by converting the rare-earth elements from primary to secondary elements and thus resolving the undermined periodicity and characterisation issues. He modified the atomic weights by a valency shift, and withdrew his claims about the rare earth—transition metal analogy.

To a large extent, the aim of this paper has been to demonstrate how bold and daring Mendeleev's statements were in 1869. At that time, Mendeleev loved to give his thoughts free rein and he had all faith in the successful future development of his system. He clearly believed in atoms and even played with the idea of an internal matter constituting these atoms (thus pointing to the complexity of atoms). In sharp contrast with Mendeleev's character in 1869, the more familiar and conservative Mendeleev of the post-1869 period was very sceptic about the possible existence of physical atoms (not to mention his disbelief in Prout's hypothesis and the complexity of atoms).[84]

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[84] Thyssen, P. "Mendeleev's Periodic Table and the 19th Century Debates on Atomism." In *Wald, Positivism and Chemistry*. Edited by M. Eisvogel and K. Ruthenberg. Würzburg: Königshausen and Neumann, 2014 (in press).

Chapter 12
Radicals, Reactions, Realism

Klaus Ruthenberg

12.1 Motivation

The scientific search for the ultimate core of physical matter is still ongoing. However, although elementary particle physics has made some breathtaking progress during the last century, almost nothing of the achieved results can be of any service for chemistry. Thus, if we may consider research in elementary particle physics – together with other fields like quantum mechanics and relativity theory – to be an enquiry into the nature of (what physicists sometimes call) matter, then chemistry obviously is not about the latter. In the first place, chemistry is about stuff, not about matter. And in order to find empirically adequate descriptions for stuff, its behaviour and properties, it is not sufficient to only look for what physics has left behind on its way to eternal matter (like the atomistic picture of the world or the energetic structuralist concept of orbitals in quantum mechanics); rather, the "turn back" to the manifest world is extremely promising when it comes to a fuller picture about chemical processes. Although most chemical radicals cannot be described as proper substances – which will be illustrated in the present study – they unequivocally count as chemical species. This is what makes them an intriguing research topic not only for chemistry, but also for the history and philosophy of chemistry. In order to give this – "intermediate" – chemical concept an adequate epistemological position, an attempt will be made here to describe one pertinent historical episode[1] in more detail: the story of the so-called "Gomberg radical" which is the very first stable

[1] I will call the period of empirical and preparative success which begins with Gomberg's work the *synthetic* period, which came after the *speculative* period and was followed by the *electronic* period of radical chemistry.

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synthetic radical compound, as main-stream modernist history of chemistry has it. Methodologically, this study consists of three main parts:

(a) Brief introduction of the historical episode (which took its start around 1900);
(b) Discussion of the chemical radical concept according to Gomberg and other contemporary chemists such as Timmermans, Walden, Ostwald, and Wald;
(c) Analysis of existence claims and the role of experimentation with respect to radicals in the framework of some modern philosophy of science as suggested by Harré, van Fraassen, and Heidelberger, respectively.

12.2 Historical Introduction

> The chemical world was moving into the twentieth century quite happily with the quadrivalency of the carbon atom and was inclined to look upon free radicals as speculative inventions. It was in this environment that Moses Gomberg's paper ›Triphenylmethyl, ein Fall von Dreiwerthigen [sic] Kohlenstoff‹ made its appearance.

In an article published in 1967, the eminent American historian of chemistry Aaron Ihde (1909–2000) used these words to describe the transition from what may be called the prehistory of the chemical concept "radical" to its early history.[2] Whereas assumptions and suggestions of nineteenth-century chemists turned out to be mere speculations, Gomberg (1866–1947) entered a field of endeavour which had better prospects empirically. Trained as an organic chemist (doctorate 1894 from the University of Michigan), he was brave enough to try to prepare tetraphenylmethane – the fully phenylated methane – in Victor Meyer's laboratory in Heidelberg (a compound Meyer himself never succeeded in synthesizing) during a research leave from his home institution.[3] Gomberg applied the cleavage of triphenylmethaneazobenzene which in fact resulted in the desired product and nitrogen as a by-product.[4] Encouraged by this success he proceeded on the path of the synthesis of arylalkanes – which he would never leave during his professional career (Ihde counts 35 papers on triphenylmethyl alone). Back in Michigan from his research journey to Europe, he made attempts to prepare – "for comparative

[2] Ihde 1967, 5. Reference is made to Gomberg 1900a, the English version of which is Gomberg 1900b. Gay 1976 offers an investigation of what is called the prehistory of the radical concept here. She critically accounts for the methodological approaches of Popper and Lakatos referring to the historical example mentioned here.

It has been suggested – to add another note referring to the history of radical theory from an extremely modernistic point of view – to consider and accept Michael Faraday as the discoverer of free radicals, see Acheson 1996.

[3] Cf. the biographical entries in Schoepfle and Bachmann 1948; Bailar 1970; Rüchardt 2000.

[4] The experimental setup is described in Gomberg 1897.

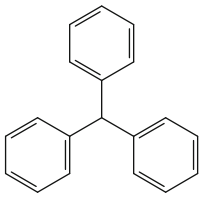

Fig. 12.1 Projected structure of triphenylmethyl. The molecule has a propeller-like shape

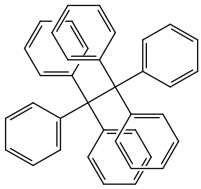

Fig. 12.2 Structure of the (virtual) hexaphenylethane

study" – the fully phenylated ethane. The chemical equation of the chosen reaction he described was:

$$2\,(C_6H_5)_3C.C1 + 2\,Ag = (C_6H_5)_3C.C(C_6H_5)_3 + 2\,AgC1$$

Still optimistic in 1900, he wrote: "Moreover, I believe that hexaphenylethane, if it had been once prepared, would turn out to be a quite stable body [ein ganz beständiger Körper]" (Gomberg 1900a, 3160). In 1914, after dozens of articles and serious discussions with many prominent chemists and contrasting with his former belief, he stated: "Hexaphenylethane still remains a figment of the imagination."[5] This is still true today.[6] In fact, Gomberg found quite fascinating reaction products, among which – at least in a solution – he assumed the radical triphenylmethyl (Fig. 12.1) but neither the dissolved product nor the solid could be identified by him.

For a long time to come, however, textbooks taught their readers that the isolated "dimer" of triphenylmethyl simply was the symmetric hexaphenylethane, which would have the following projected structural formula (Fig. 12.2)[7].

However, it remained unclear what exactly the reaction product of Gomberg's attempt to bring together two monomers of triphenylmethyl really was until 1968, when new results suggested a quinoid structure.[8] Crucial for this scientific progress was the application of nuclear magnetic resonance spectrometry (^{1}H-NMR). With the latter, twenty-five "aromatic", four "unsaturated or dienic", and one "saturated" hydrogen atoms could be differentiated in samples of "Gomberg's" solid (Sykes 1986, 44).

[5] Gomberg 1914, 1156.

[6] In his well-known textbook on reaction mechanisms, Peter Sykes states: "Hexaphenylethane has not, indeed, ever been prepared, and may well be not capable of existing under normal conditions due to the enormous steric crowding that would be present." (Sykes 1986, 301)

[7] C.f. Fieser and Fieser 1968, 410.

[8] See Lankamp et al. 1968. See also Nair et al. 2006.

12.3 What Went Wrong?

Besides the very small yield the product showed unexpected properties: a high reactivity, the behaviour of unsaturated compounds (like adding halogens easily), the colored appearance, the easy, seemingly reversible peroxidation when brought into contact with air (oxygen), and worst of all: the elemental analysis resulted in 88 % carbon and 6 % hydrogen, contrasting the theoretical values of 94 % C and 6 % H for $(C_6H_5)_6C_2$. Rather than the desired hexaphenylethane Gomberg had indeed synthesized (among others, facing the tiny yield) a compound that showed many similarities with what could have been assumed for the so far unknown triphenylmethyl, $(C_6H_5)_3C$. The latter could be considered the "monomer" of (the "dimer") hexaphenylethane, and had to be considered a *radical*, that is – with respect to the contemporary theories – a chemical entity with an unsaturated, trivalent carbon atom. It has to be pointed out, however, that Gomberg did not isolate this compound in a proper sense.

The concept of a chemical radical was introduced by Antoine Lavoisier (1743–1794), who attributed it to the assumed crucial parts of acids. Jöns Jacob Berzelius (1779–1848) used the word in the meaning of an "element imitator" – that is, as a virtual ordering principle.[9] Chemists have been contributing to the radical research ever since (cf. the historical surveys in Walden 1924; Gomberg 1932; Ihde 1967; Rocke 1984; Rüchardt 1992; Nye 1993). In a survey of free radical chemistry Gomberg himself gave the following historical summary on radicals leading up to his work on the "perphenylated" ethane (Gomberg 1932):

1815–1835	Radicals were agencies for classifying the increasing number of organic substances
1835–1850	It became apparent that the analogy between radicals and elements was merely formal
1848–1858	The type theory came into being
1860–1900	Valency theory and the quadrivalency doctrine for carbon emerged.

In today's chemistry – as opposed to the early historical phase featuring Lavoisier and others as well as to the time of Gomberg's original contributions around 1900 – a radical is defined as a particle (atomic or molecular) which contains unpaired electrons. There is no doubt among modern chemists that (some) radicals do exist in a substantial, literal sense, although most of the latter are quite unstable or show only very short lifetimes.[10] For Gomberg and his contemporaries the

[9] Cf. in the preface of his chemistry textbook Berzelius 1825.

[10] Well-known examples (from modern chemistry) are the nitrogen oxides NO and NO_2. The most fascinating exception of the group of instable or intermediate radicals is dioxygen, O_2. The molecules of this (normal) allotrope of oxygen contain two unpaired electrons and are reasonably stable. Accordingly most modernist attempts to set up a historical order for the development of the radical concept look like the following of Rüchardt 1992: 1787–1900 Period of the clarification of notion; 1900–1945 Period of discoveries; 1945 – today Period of theoretical achievement and successful application. In another article the same author even classifies a single electron as radical (Rüchardt and Mayer-Ruthardt 1969, 41).

break of the quadrivalence doctrine was the main criterion for a substance to be classified as a radical. Consistently, he used the notion "radical" right from the start of his investigations.[11]

Although Gomberg not only failed to synthesize the desired entity, and although he initially characterized the found products incorrectly and incompletely – the substance he found was actually the dimeric peroxide[12] of triphenylmethyl – he eventually found his path into a distinguished professional career because he systematically and steadily kept working in that field which he entered – by chance. The main concern of his research concept from 1900 on was the proof of the possible trivalency of carbon atoms rather than to install radical chemistry (as modern chemistry has it[13]). He even used the careful term "radicle" in his Gomberg 1901 which was used to address molecular groupings (like "methyl", CH_3, in methylchloride or "methylen", CH_2, in methylenchloride), at least if we follow Ostwald's *Grundlinien der Anorganischen Chemie* from 1900.[14] "It was against this background of uninterrupted progress [using the hypothesis of quadrivalent carbon atoms in synthetic organic chemistry] that for almost half a century a publication appeared with the startling title ›Triphenylmethyl, an Instance of Trivalent Carbon‹. The original intention of the experimenter was to prepare a new substance of the composition $(C_6H_5)_6C_2$ . . ."[15] More than 10 years of scientific argument were necessary before the concept of what was called "free radicals" – although only very few of them could have been characterized or isolated – was accepted in the community of organic chemists.[16] As to the main arguments for this acceptance, Gomberg mentioned particularly two: the "hexaphenylethane riddle",[17] that is the problem of the impossibility to prepare this compound, and the successful synthesis of the trisbiphenylylmethyl radical by Wilhelm Schlenk in 1910.[18] The latter compound showed comparable properties like the Gomberg "radical" and thus helped to foster the central hypothesis. Finally, Gomberg claimed the following:

[11] From a modern point of view the trivalency is not a prerequisite for a radical status of a substance. Carbon monoxide, CO, for example, is described as having a triple bond in quantum chemistry, and nevertheless it is not a radical (e.g. it is diamagnetic in the ground state).

[12] The formation of which is reversible (expressed by color changes). $(C_6H_5)_6C-O-O-C(C_6H_5)_6$ comes to 88.0 % C and 5.8 % H.

[13] Gilbert Lewis (1875–1946) seems to have introduced the radical concept of unpaired electrons and the paramagnetism of such radicals (Lewis 1923).

[14] Note that the original "Radikal" with the description referred to here was translated into "radicle", see the 2nd ed. (Ostwald 1904, 406).

[15] Gomberg 1928, 163. Presumably Gomberg's formulation inspired Ihde when he wrote his statement cited at the introduction of the present contribution.

[16] Gomberg gives an account of this scientific struggle in Gomberg 1914. That paper is the first in which he used the expression *radical* in a title.

[17] Cf. the title of McBride 1974.

[18] A surveying account of work and life of Wilhelm Schlenk is given in Tidwell 2001.

"Hitherto, the definitely recognized units in chemistry have been: atoms, molecules, ions, and electrons. And now, in addition to these four, chemistry, it seems, has to take into account a fifth entity – free radicals."[19]

Hence, nothing went wrong as far as Gomberg was concerned – except that he had not found a free radical.

12.4 What Is This Thing Called Radical?

In what sense can a radical be called a substance or a material carrier of chemical change? Obviously, radicals do not fit into imaginable general schemes of chemical stuff. At least they do not in every respect that might be considered typical for usual manifest material. Joachim Schummer, for example, discusses an "experimental stuff hierarchy" (Schummer 2008, 13). According to this classical hierarchy, chemical work starts with heterogeneous mixtures and proceeds analytically[20] to chemical elements via homogeneous mixtures and pure compounds. Gomberg's radical surely is a compound and not an element. Whether or not "it" – in the solid state – was heterogeneous or homogeneous, however, was not possible to decide for Gomberg. Because its chemical identity had been not yet discovered, the purification of the obtained material, be it solid or dissolved, had to be performed by trial and error.[21] Hence, an assignment of Gomberg's stuff according to classical substance systems hardly seems possible.

In order to find the epistemological place of the concept of radical in Gomberg's days it is useful to apply different theoretical approaches from chemistry and the heritage of the historically oriented philosophy of science. The over-arching approach we shall refer to here is the *stuff* notion; since at least the late eighteenth century, chemistry has been characterized as the enterprise concerned with the property changes of stuff by most of its practitioners. The Belgian chemist Jean Timmermans (1882–1971), for example, who was concerned with standardization topics in chemistry in an international framework, gave the following practically motivated list of questions as a general outline for his book on the general characterization of chemical species: "(1) How may a given physical-chemical system be defined without ambiguity? This is the problem of chemical species; (2) How may such a system be realized? This is the problem of pure materials;

[19] Gomberg 1928, 164. In his monograph on philosophy of chemistry, the Dutch philosopher Jaap van Brakel refers to a similar view. In a footnote referring to discussions of USSR philosophers of chemistry such as Kedrov he states: "Here, the material carriers of chemical change are assumed to be atoms, molecules, radicals and ions (both of atoms and atom groups)", van Brakel 2000, 25.

[20] Note that in fact any analytical work incorporates necessary synthetic steps, that is, the "analytical" methodology like in Schummer's description should be read *theoretically* rather than *empirically*.

[21] Note that this is the case for many pure substances, for example the chemical elements during the very first occasion of their discovery or preparation.

(3) How may its constants be measured with precision and exactitude?; (4) How may the best method of purification and the most probable value of the constants of pure materials be found in the literature?"[22]

Trying to address at least the first three of these questions we can collect the following list of empirical information from Gomberg's original work (according to Walden 1924, 49–52, who not only refers to the original publication, and takes into account results of other scientists):

(a) triphenylmethyl is unsaturated which is confirmed by the reactions with oxygen (yielding the peroxide) and iodine (yielding the iodide)
(b) despite its extremely unsaturated character triphenylmethyl seems to have a double formula in solution (with respect to osmotic molecular mass determinations)
(c) with compounds containing oxygen like ethers triphenylmethyl builds additive structures (Walden 1924, 50: *Molekülverbindungen*)
(d) similarly, it yields addition products with nitriles (R-CN)
(e) with "indifferent" solvents (chloroform, carbon disulfide, benzene, toluene) addition products were built, too
(f) the "free" triphenylmethyl can be considered a basic radical (*basisches Radikal*) because it has a good electric conductivity in SO_2 solutions
(g) particularly remarkable is the formation of addition products even with totally saturated hydrocarbons like hexane, heptane, octane, decane, cyclohexane
(h) similar results are obtained with triarylmethyls other than triphenylmethyl
(i) triphenylmethyl is reasonably resistant against hydrogen and water
(j) hydrogen chloride (HCl, in dry benzene) causes a rearrangement to p-benzhydryltetraphenyl methane

According to this list, the characterization of Gomberg's product follows classical observable chemical properties such as color, melting point, and, most important, the *reactivity* (which is inferred from the change of color, the state of aggregate, stability, solubility, conductivity, and the like). Additionally, he applies instrumental devices like the thermometer, the balance, the elementary analysis apparatus and the photometer. In what can be considered his final and concluding published statement on the triphenylmethyl story he mentions the following items as "properties of the free radical": stability, color, disproportionation, molecular combinations, irreversible combinations and chemical reactions; Gomberg 1932, 446–447. However, the reliability of his measurements was very remote from that usually obtained for stable substances. The cryoscopic molecular weight determinations, for example, varied from 412 to 532, with an average of 477. Hence, there was no way to conclude that the solid really was "pure" triphenylmethyl which had a calculated molecular weight of 243. Moreover, the dimer with a theoretical molecular weight of 486 was closer, but by no means a good match. Despite this mismatch and the obviously incorrect first claim that the obtained solid was a

[22] Timmermans 1940, 5.

radical, Gomberg postulated the following equilibrium (Cf. Gomberg 1928, 163, and Ihde 1967, 7):

$$\{(C_6H_5)_3C\}_2 = 2(C_6H_5)_3C$$

As we have emphasized already, Gomberg's foremost approach to the characterization or *proof of existence* of his triphenylmethyl was based on *reactivity*. During all these attempts he did not succeed in meeting the customary criteria like those formulated at approximately the same time by Timmermans. Any of the first three questions published by the latter must remain unanswered. However, though the attempts to *identify* his solid and dissolved products ended up in more or less plausible suggestions we can conclude that his empirical descriptions were more than just lucky guesses. He not only found his own area of research and – because he was a gifted, tenacious and prolific experimenter – owed his reputation and fame; he also initiated an international research program which was devoted to the search for stable free radicals.

Most speculative radicals of the nineteenth century, like benzoyl, cacodyl, ethyl or acetyl (some of which later turned into formal-descriptive "rests" or "functional groups") had no chance to become real entities, or better, to be given an empirically adequate description.[23] The Gomberg radical, in contrast, became more than just some strange movement behind the curtain.

In the first place the reference to the concept of stuff is a macroscopic view, a view very close to or rooted in the manifest world.[24] There are early attempts to describe chemical substances and their changes without reference to a particle picture but in an empiricist or operationalist attitude. Wilhelm Ostwald (1853–1932) was among those who were skeptical of metaphysical assumptions in general and with speculative atomism in particular. He claimed that a recognized chemical substance must be capable of being isolated as a stuff sample. In his book on electrochemistry from 1896 he wrote:

> It took a long time before it was finally recognized that the very nature of the organic radicals is, inherently, such as to preclude the possibility of isolating them. And now it is becoming evident that the same holds true of ions.[25]

According to Ostwald, any metaphysical assumption about unobservable or undetectable entities (atoms, molecules, ions, and radicals) should be avoided.

[23] Here of course reference is made to Hacking's *entity realism* and van Fraassen's *constructive empiricism*. We will return to both later. – It has to be noted that the mentioned ethyl radical – at least what might be called its empirically adequate correlate – eventually came into life in the 1930s, when Friedrich Paneth and his co-workers arranged to have determined short-lived methyl and ethyl radicals in ingenious experimental set-ups (Paneth and Lautsch 1930). This intriguing story and its specific philosophical background will be discussed elsewhere.

[24] Van Brakel stresses this classical empiricist claim in his textbook van Brakel 2000.

[25] In his survey, Gomberg, referring to the "uninterrupted progress" of fixed quadrivalence of carbon, cites this passage (Gomberg 1932, 443).

In his *Prinzipien der Chemie* from 1907, he (not without conceptual problems[26]) described the dissolved ions in a solution of (simple) salts as isomers of the respective elements (e.g., Na^+/Na and Cl^-/Cl), and addressed these entities using the singular form (that is, e.g. *chloride ion* instead of *chloride ions*). In contrast to the huge amount of empirical results from electrochemistry – to which he had contributed largely – there was no information available in the field of free radical research at the time Ostwald wrote his *Elektrochemie*. Hence, he felt justified to argue against the purely speculative radical concept which had – as far as he was concerned – by no means led to new knowledge, new research, or new substances.

In his theoretical arguments, Gomberg referred to a submicroscopic picture in two main respects. Firstly, he was trying to find an experimental proof for a stable *trivalent* carbon atom (after having recognized this very possibility in his attempts to synthesize hexaphenylethan, as it were). This particular projection of the elementary distribution to the unobservable particle world was his first aim and to him it meant a radical status because all organic radicals discussed in the nineteenth century (e.g., ethyl and acetyl) consisted of trivalent carbon atoms. Secondly, he was applying the notions *monomer* and *dimer* in a molecularistic sense. These notions imply a submicroscopic point of view, at least in this case. Although he occasionally addressed his solid reaction product as "radical", Gomberg considered – and was forced to consider by his molecular weight determinations – this solid to be something assembled from the monomers which he assumed to exist in the dissolved state. However, Ostwald's general criticism against any form of speculation regarding the properties of atoms or molecules does not hold referring to Gomberg's work: the latter had something substantial in his hands, and he was able to determine some classical "constants".[27] Even another classical concept to operationalize the classification of substances by Ostwald, the *stuff law*, does not apply easily to radicals.[28] If stuff constants only are obtained with extraordinary high variations (e.g., the molecular weights), and if these constants cannot be assigned unequivocally to one entity (e.g., the colored solutions and the uncolored solid) alone, then this *stuff law* does not seem to be in force at all for this example. If a solution of Gomberg's "radical" is used for some measurement, then something related to but different to the solid is addressed. In that respect Ostwald was right to point at the similarity of salt solutions on the one hand and radicals (triphenylmethyl and its "dimer") on the other, but his *stuff law* is hardly applicable to radicals.

[26] Cf. Ruthenberg 2008b for a short discussion of this episode from the history of the philosophy of chemistry.

[27] The author has not found an explicit reference of Ostwald's to Gomberg's radical. In his *Principles* from 1909, Ostwald still referred critically to the expression *radical* as a formal and structural grouping concept without mentioning concrete examples (Ostwald 1909, 325).

[28] Ostwald said that if two bodies have some specific properties in common then all other specific properties will turn out to be identical, too: "…wenn bei zwei Körpern einige spezifische Eigenschaften übereinstimmen, dann erweisen sich auch alle anderen spezifischen Eigenschaften übereinstimmend." (Ostwald 1907, 74–75)

Another example of an empiricist[29] and operationalist approach to chemistry is the theory of the Bohemian Chemist František Wald (1861–1930). In his article "*Was ist ein chemisches Individuum*?", Wald said:

> Chemical individuals are phases that occur in a phase system with at least one independent variation, and retain evidently consistent for all variations associated with the conditions of the phase system.[30]

Phases are characterized by Wald, for example, as follows: "In brief, with the word *phase* we denote any part in a mixture in equilibrium that is perceived by the senses, and that is a *homogeneous* part, *distinguishable* from another part."[31] As to triphenylmethyl, the preparation and comparison of different aggregate states is extremely restricted. The dissolving, for example, leads to higher extinctions in calorimetric measurements if no shielding gas is applied because the reaction with oxygen is very quick. That means, because triphenylmethyl cannot be obtained consistently for all variations of the observed phase system (that is the variations through the states of aggregation) and because it (what?) cannot be perceived easily by the senses and because for Gomberg it was not clear whether or not the obtained substance was in equilibrium, it cannot be considered a *chemical individual* proper according to Wald. Most radicals – if we take into account the current chemical knowledge – are short-lived intermediates and cannot be prepared and handled like common stuff samples and therefore can hardly be described in terms of a phase conception or a macroscopic approach to stuff. Nevertheless Gomberg's radical and all the other examples are chemical species, which is supported by the view of Jaap van Brakel (unless the latter does not refer to the Gomberg story):

> Chemical species which cannot be put into bottles, cannot be subjected to any reversible phase transition, occur only in solutions or other special environments, have an extremely short half-life, only "exist" in excited stages, etc., may have a full claim to being a chemical species and may even claim to be a separate phase, but may or may not claim to be substances. If the species only exist in equilibrium with other species "inside" pure substances or solutions, it seems plausible to admit them as species, but not as substances. This includes radicals, reactive fragments, activated complexes, ligand-receptor complexes, etc. Whether (different kinds of) tautomers should be classified as separate substances or species is less obvious. (van Brakel 2012, 222)

Obviously the classical macroscopic approaches – at least in the versions of Wald and Ostwald – do show disadvantages because of the unnecessary restrictions to phases and stable preparations. In the following we shall try to find other approaches which might throw some more light on the epistemological status of the radical concept.

[29] Cf. van Brakel 2013.

[30] Ruthenberg 2009, 75–76.

[31] Ruthenberg 2008a, 59 (emphases original).

12.5 The Existence of Radicals as Problem of Scientific Realism

As to the central statement of *scientific realism* Bas van Fraassen cites Wilfrid Sellars as follows: "To have good reason to accept a theory is to have good reason to believe that the entities it postulates are real."[32] Existence criteria might be formulated scientifically like the Latvian-German chemist and historian of chemistry (and former student of Ostwald) Paul Walden (1863–1957) communicated in his monograph on radicals from 1924. He differentiated three possible cases:

1. radicals are *preparable* chemical individuals [*isolierbare Individuen*] bearing all properties of free and stable molecules [*freier und beständiger Molekeln*], or, contrasting this,
2. radicals are *not preparable*, but occur intermediary as unsaturated fragments of molecules which react with each other in order to come together immediately to build more stable chemical entities as end products, or
3. radicals do exist in our imagination only but not as stuff kinds [*Stoffarten*]; mentally we consider them to be aids in the interpretation of chemical reactions.[33]

Hence, according to Walden, the radical concept in chemistry has a continuous history: he used the same term, be it in a theoretical sense or in an empirical context. The bridging idea is obviously that of something unsaturated in the sense organic chemists gave this property at least since the nineteenth century. This "unsaturated something" is imagined as a structural or substantial entity which is part of a (or several) more stable structure(s) or substance(s). Intriguingly, Walden described Gomberg's triphenylmethyl as a radical of the first kind, although he discussed all the "classical" problems addressed in the present study in detail. In fact, the free radical triphenylmethyl (which is the reference of the structure shown in Fig. 12.1) cannot be prepared. Rather it exists in solution only where it carries some stabilizing ligands.

As we have already seen, Gomberg as well considered his radical to be an existing, real entity that is he believed that he had found an example of a trivalent carbon compound.[34]

A very useful threefold scheme for the taxonomy of scientific theories and entities from a realist point of view has been proposed by Rom Harré.[35] According to Harré, *type 1 theories* are cognitive objects with pragmatic properties which refer to observable entities like snooker balls, the planet Mars, mammal livers, *type*

[32] van Fraassen 1984, 250.

[33] Walden 1924, 3

[34] See, for example, Gomberg 1925. Even more so in modern scientific papers: "The experimental demonstration of the existence of the triphenylmethyl radical by Gomberg is a milestone in the development of mechanistic organic chemistry." (Nair et al. 2006)

[35] The author writes: "I believe that science disposes of three different methodologies, each appropriate to the study of a specific domain of beings, both natural and cultural." (Harré 1986, 70)

2 theories are cognitive objects with iconic properties referring to picturable but presently not observable entities like bacteria and X-ray stars, and *type 3 theories* are cognitive objects with mathematical properties which refer to non-picturable and unobservable entities, like neutrinos and quarks.[36] According to Harré's scheme Gomberg's substance – particularly the solid – seems to belong to the type 1 entities – at first sight. Taking a closer look we realize that this object-centered view might lead to a distorted picture of the chemical stuff which this substance is: the solid is observable but not a radical, the dissolved material is no longer observable but might be (and is) described as radical. Thus, if we try to address this entity which tentatively is assigned as radical we could denote it to the type 2 entity kind, and the relation of the two Gomberg described as a chemical equilibrium.

What seems to be peculiar for chemistry is the priority of entity-realism over theory-realism: long before an appropriate theoretical representation was developed chemists denoted their scientific objects as radicals. To put it in other words: the discovery of "triphenylmethyl" has not been the result of theory-driven activities.

After the "anomaly period" initiated by Gomberg the whole community of chemists slowly took over the belief in radicals both as *theory* (*truth*) *realists* and as *entity realists*. Chemists began to believe in the existence of free radicals because Gomberg and others could present evidence for a *single bond trivalency* of carbon atoms in one very special case (and later for related or derived cases as well). Trivalency alone of course is not a necessary condition for a radical configuration, see the (to use modern terms) double and triple bonds in hydrocarbons and carbon monoxide, CO. As to triphenylmethyl, however, trivalency must result in three single bonds at the central carbon atom and this conclusion destructs the constant valency concept. However, the growing belief of the chemical community did indeed refer to the contemporary radical concept. This concept was dominated by the valency theory in general and the quadrivalency doctrine in particular. At least the trivalency part of Gomberg's results, which was a surprising "amendment" of the old point of view, has been accepted after many experiments and hard discussions. There was no reason to skip quadrivalency in general, but after 1900 we observe a decreasing support of the former canonic view that carbon atoms *must* comprise four bonds in their molecules. Only very few worried about the "down-grade" of their former belief which in fact was considered as an accommodation of theory to empirical facts rather than a revolution.[37] If – in a Kuhnian sense – a part of the described historical episode is to be called a *crisis*, it is the very part of the difficulties to find a proper characterization for the reaction products. In retrospect, it certainly was a breakthrough and after the new concept was established and new research directions opened the old normal science proceeded. Although Gomberg's

[36] Harré 1986, 70–71. The author claims that the vast majority of scientific theories are of type 2.

[37] A fact that lets the approach of constructive empiricism of Bas van Fraassen appear sympathetic, because to care for empirical adequacy is less ambitious than to change his or her belief whenever a theory develops or changes. Cf. van Fraassen 2001.

main aim in the first place was just to synthesize a new compound, and then to find evidence for trivalency rather than to find a stable radical and establish the revised radical theory, at least one thing had become common knowledge in chemistry: there are radicals out there, which in certain aspects, e.g. structurally, fit to the old hypotheses, and some of them can even be characterized empirically. About 20 years later theoretical chemists invented their version of radical theory which was alien to the former versions of the nineteenth century (but not entirely incompatible) as it were[38]: a quantum mechanical description of electron configurations comprising unpaired, "anti-bonding" ("radical") electrons.[39]

12.6 Radicals as Public Hallucinations: The Role of Experimentation

So to speak, the triphenylmethyl radical and, for comparison, the methyl radical[40] are situated at the opposite ends of a virtual scale from empirical to theoretical substances or *observable* to *unobservable chemical species*[41]: methyl can only be subjected to experiments if very specific conditions are set by the instrumentation, whereas triphenylmethyl (and its relatives) in principle can be studied by classical means (e.g., "wet chemistry") and – at least in principle – by using unaided human senses. To find out more about the epistemological status of the radical concept it is therefore necessary to analyze the particular experimental situation.

Michael Heidelberger suggests a taxonomy of roles of (instrumental) experimentation.[42] According to this functional taxonomy, there are two basic types of experiments, those to improve or expand knowledge and those to adjust actual knowledge to a theoretical context. The first type can be differentiated into a productive, a representative, and a constructive or imitative function. *Productive* is an experimental setting that produces phenomena which usually could not

[38] The radical concept has run through several significant changes (for discussions of the nineteenth century developments see Gomberg 1932; Gay 1976; Rocke 1984). Therefore it is questionable to speak about "the one" radical theory due to "translation" problems (not to speak of possible incommensurabilities). There is indeed no significant sense to describe this history as linear story of success (as textbooks and modern literature sometimes do).

[39] Early theoretical works in the twentieth century are Pauling and Wheland 1933; Hückel 1934; Ingold 1934. Intriguingly, the latter explicitly discusses "chemical" vs. "physical" explanations of the radical phenomenon. The first account of unpaired electrons in radicals and their paramagnetic properties was published by Gilbert Lewis (1923).

[40] Cf. Paneth and Lautsch 1930.

[41] I apply the terminology of Bas van Fraassen here. According to the latter, the expression "observable" refers to unaided acts of perception only and is object-related (e.g., van Fraassen 2001). Hence, and contrasting for example Hacking 1981, the use of even the smallest lens or optical microscope yields *representations*.

[42] Cf. Heidelberger 1998, 2003.

be observed (examples: air pump; particle accelerator), *representative* we call instrumental techniques that transform one phenomenon into another (examples: clock; thermometer), and *constructive* (or *imitative*) experiments are made to present the phenomenon in a "pure" form in order to mimic nature (examples: lightning simulation; cloud chamber). One main conclusion Heidelberger draws from his investigations in the history and philosophy of experiment is that the nature of experimental attempts lies not solely in the testing of theories (like earlier philosophies of science – verificationism and falsificationism – have suggested) but in the *making of reality*.

How does our historical example fit that scheme? Obviously, Gomberg's early preparative experiments have been entirely *productive*. There is no doubt that *all* synthetical experiments in chemical research are performed to produce new stuff or new phenomena or chemical species. However, particularly in this case, the production of reality has a more "intrinsic" character, because the amount and influence of the instrumental experimentation is rather low. In order to perform a chemical process it is necessary to bring the reaction partners into the same reaction space and produce or provide favorable conditions. As to the *Gomberg radical*, the really new aspects came into the world by the ingenious choice of – though already well known – reaction path and reaction parameters by the experimenter. We should not forget that methods applied to identify the material products, like melting point measurements and elemental analysis, are part of the whole methodology and of course belong to the *representative* section of experimentation.

An intriguing and inventive description of the interrelations between certain observations and their correlates was given by Bas van Fraassen. Discussing Heidelberger's suggestions, van Fraassen adds a (virtual) device to imitate rainbows to the list of constructive experiments (2008, 94). In Chap. 4 "A Window on the Invisible World (?)" he uses the rainbow phenomenon as a central example for what he calls "public hallucinations", which are assigned as entities that cannot be represented as things, but are all the same not purely subjective (2008, 105). From our analysis of the radical concept referring to the Gomberg episode it becomes clear that triphenylmethyl, like many other – even modern – radicals cannot be represented as substances. Nevertheless they are extremely interesting and describable in systematic, empirical ways. Hence it is tempting to use van Fraassen's label and call these radicals *public hallucinations*.

12.7 Concluding Remarks

Summing up this study of the epistemological status of chemical radicals of the *synthetic* period with respect to historical development the following aspects seem notable. To begin with the more systematic topics: Firstly, the classical (or phenomenological or thermodynamical) approach of stuff characterization appears not to come to terms with the chemical species radical in general. Only few exceptions are stable enough under normal conditions and can be observed,

analyzed, characterized or represented along the lines of the methodology of the stuff (or phase) concept. On the other hand, classical definitions like "Chemistry is the science of stuff and its changes"[43] still hold when applied to radicals, if the emphasis is laid on the last word: what in fact is registered or detected during chemical experiments are stuff *changes*. It has to be emphasized that radicals are nevertheless intriguing chemical research objects. Secondly, most chemical radicals are *unobservable*, a few others, like triphenylmethyl and its relatives are more stable and therefore do exist as substantial free radicals. Unobservable radicals are not as abstract as neutrinos or basic substances (atomic nuclei). Their status depends much more on their lifetime and chemical stability. Thirdly, the experimental situation can be considered as *productive*, that is it produces new phenomena and new entities. Fourthly, the notion *preparation* which is an experimental notion and obviously similar to *production* and *construction* to certain respects offers another intriguing path of interpretation particularly when it comes to chemistry. Considered as a set of operational steps followed by the experimenters, preparation appears to be a correct description not only for radicals but for any other chemical sample, as well. Following this, the radical research and its history and philosophy can as well throw some light on our understanding of general chemistry.

In addition to these more or less systematic aspects there of course are some historical points to make: Firstly, it has to be pointed out that, inferred from the described historical episode, not any anomaly and not any crisis lead to a revolution or paradigm shift. Obviously, Gomberg's work is situated in the middle of a *normal* phase of what might be characterized as *molecularistic organic chemistry* which began in the nineteenth century, and which is still in place. The acceptance of free radicals at best was something of a *local theoretical turnover*. Secondly, it is nevertheless amazing, how (organic) chemistry adapted the news: Although the first speculative period was already accepted as being over, Gomberg and his followers in the research program managed to retrieve some pieces of the original concept and filled this with new life. Obviously, the first radical concept by Lavoisier was flexible enough to tolerate significant changes. Even the entirely new electronic theory of valency (which was not addressed in detail here), brought forward by Gilbert Lewis and the quantum chemists, was simply absorbed by this extraordinarily vivid chemical concept.

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[43] Meyer and Rimbach (1921): "Die Chemie ist die Wissenschaft vom Stoffe und seinen Änderungen."

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Chapter 13
Orbital Symmetry, Idealization, and the Kairetic Account of Scientific Explanation

Grant Fisher

13.1 Introduction

Idealization plays an important function in scientific modelling and chemistry is no exception. Models in chemistry often distort key factors of their target systems in order to facilitate the calculation of molecular properties, represent key aspects of molecular dynamics, and the prediction of the stereochemical course of chemical reactions. But the idea that idealized models *explain* their target systems poses a significant problem. Since idealized models are literally false in crucial respects, they don't count as veridical explanations and hence it would seem that they fail to legitimately "explain". Given that idealizations are widely employed in the sciences generally, if one accepts that explanation is a key goal of scientific inquiry including chemistry, then something needs to be done to rehabilitate explanatory idealization.

The focus of this chapter is Michael Strevens' (2008) *kairetic account* of scientific explanation, which offers an interesting solution to the problem of explanatory idealization. In its most general terms, Strevens claims that the scientific explanation of events and regularities consists of a process of abstraction away from detailed, veridical causal models in order to generate causal models that contain only those factors that make a difference to the causal production of the explanatory target. Strevens' approach to idealized explanatory casual models is simply to assert that while idealizations are literally false, they distort only *non*-difference-makers. Hence they do not misrepresent the explanatorily relevant causal factors that

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causally entail their targets. In so doing, idealized causal models can serve a cognitive function by raising awareness of those factors that are not relevant to our understanding of a phenomenon's occurrence.

In spite of the considerable virtues of Strevens' account of scientific explanation, this chapter makes the case that it fails to adequately capture the nature and function of explanatory idealization in chemistry. Explanatory idealization in chemistry is often a matter of distorting explanatorily relevant causal factors – the difference-makers themselves. Strevens' commitment to an ontological conception of causal explanation rules out the idealization of difference-makers because they undermine the causal entailment of the target phenomenon. And in an ontological mode of explanation, it is difficult to see how idealized models in chemistry could perform a legitimate causal-explanatory function. For example, the ontological status of atomic and molecular orbitals is vexed to say the least and therefore appear to be poor candidates for causal-difference-makers in Strevens' sense.

This chapter argues that some of the most important developments in the quantum chemical modelling of reaction mechanisms may well distort the causal story but they cite *non*-causal factors that make a difference to their explanatory targets. The development of molecular orbital approaches to the study of an important class of organic reactions – pericyclic reactions – provide selection rules based on the *symmetry* of the molecular orbital wave functions contributing most to a given chemical reaction in their class. Symmetry, it is argued, is a non-causal difference-maker. One can provide a positive explanatory function for idealized models even if those models distort our understanding of the *causal* production of the target phenomenon. Thus one can retain the difference-making criterion of explanatory relevance so long as one is prepared to accept that not all explanation is causal. Strevens himself suggests that one *might* detach difference-making from causal explanation but he does not pursue this for obvious reasons.

13.2 Causal Difference-Making and Idealized Models

Strevens defends the idea that scientific explanation is a matter of constructing models citing causal factors that make a difference to the causal production of an event or regularity.[1] A casual factor must play an essential role in (say) an event's occurrence in order to count as a causal difference-maker. This means one cannot remove the factor without invalidating the "causal entailment" of the target – the logical derivation representing the actual target's causal production (2008, p. 72). This requires a "setup" specifying laws, events and background conditions and

[1] I focus on Strevens' ideas concerning explanation in deterministic systems.

the entailment or derivation itself is what Strevens calls the "follow-through" representing the actual causal processes resulting in the target's occurrence. The kairetic account specifies a procedure for determining these causal difference-makers. One begins with a detailed, veridical physical model of a given explanatory target and the idea is to extract a more abstract model shorn of its causal irrelevances. If explanatorily irrelevant causal factors can be eliminated, or better if we can remove some of the detail (for example, by replacing a parameter's definite value by some bounded range of values), or optimized (maximally abstract, i.e. as general as it can be) without invalidating the causal entailment of the explanandum, then those factors are explanatorily irrelevant and hence play no part in our understanding of the target phenomenon.

By following the kairetic procedure one ends up with an "explanatory kernel" – a model in which all the factors are difference-makers (ibid, p. 88). Ultimately, the aim of the kairetic procedure is what Strevens calls a "standalone explanation" (ibid, p. 117). These models should be complete in the sense that none of the causal difference-makers are missing, and cohesive in the sense that that they cite causally contiguous factors, meaning that they do not include different kinds of causal elements. This is one of the trickier desiderata of the kairetic account because it requires a means to individuate relevantly similar causal elements. I will not be concerned with this specific issue here, suffice to say that Strevens appeals to the level of fundamental physics in order to individuate causal contiguity (see pp. 104–109). Similarly, Strevens appeals to fundamental physics to cash out the completeness of standalone explanations such that they issue in "deep" scientific understanding. This commitment will be discussed below.

Both event and regularity explanation (the explanation of causal laws or generalizations) evoke causal mechanisms because a mechanism which explains a law also explains any instance of the law. And the kairetic procedure operates in the same way in regularity explanation as it does in event explanation. Having said that, regularity explanation requires some additional conceptual apparatus. Strevens' sense of "mechanism" is broad because it covers any causal difference-making process and operates in roughly the following way: a causal law of the form *If F*, *then G* expresses a causal connection between *F*-ness and *G*-ness, which is explained by citing a causal mechanism upon which this connection depends (ibid, pp. 222–223). A causal model explaining a law is essentially an argument logically entailing all events instantiating the law to be explained (ibid, p. 224). It consists of a causal model's follow through realised by any concrete instance of the law, where the setup comprises "a specification of the particular facts in virtue of which the process in question realises the schema" (ibid, p. 225). One doesn't explain a law or generalization itself by evoking a mechanism. The explanatory target is usually the property *G*-ness, since one is providing a mechanism – the difference-making process – that connects *F*-ness and *G*-ness. Further, the explanation of a causal law or generalization by a mechanism schema is essentially the explanation of the high-level properties of the generalization to be explained by those of fundamental physical laws. However, providing a mechanism is not a sufficient condition for explanation. One will invariably

draw on what Strevens calls a "basing generalization", which expresses the existence of a contingent pattern of phenomena required to casually entail the explanatory target.[2]

This brief synopsis of Strevens' account of scientific explanation hardly begins to do justice to the power and comprehensiveness of his ideas. And while the focus of this chapter is relatively narrow because it is concerned with idealized explanation, this is nonetheless an important and revealing aspect of his thinking on scientific explanation. Idealization arises in the context of regularity explanation and is "any misrepresentation of the causal process that improves the explanatory power of a model by comparison with its veridical counterpart" (ibid, p. 300). The explanatory power of idealized models is to be assessed relative to a "veridical counterpart": a model that has not been subject to the kairetic procedure of optimization. Since it hasn't been optimized, a veridical counterpart falsely implies that *non*-difference-makers as well as difference-makers are explanatorily relevant. To say that idealization *improves* explanatory power relative to its veridical counterpart might, however, sound counter-intuitive because idealized models distort the causal story. But Strevens' tactic is simply to assert that idealizations are not to be taken literally; they should not be taken as implying that *non*-actual properties are causally relevant to the production of an event or regularity. Rather, they draw our attention to the fact that some actual property, while causally salient, is a non-difference-maker. An idealized model will only distort some subset of *non*-difference makers, and what remains are only those causal factors that make a difference to the explanatory target. Therefore an idealized model has more explanatory power than its veridical counterpart because it does not contain an excess of explanatory irrelevances.

More provocative is Strevens' claim that "[a]n idealizing explanation is in one important respect explanatorily optimal: it cannot be further improved" (ibid). Idealized models explicitly communicate the idea that certain features of a system do not make a difference to the causal entailment of the explanandum. Compare idealized models to what Strevens calls a "canonical model", which is a causal model that has been subject to the kairetic procedure of optimization and contains

[2] For example, in order to explain why all normal ravens are naturally black, it is not enough to posit a mechanism described by a causal model that cites the relevant biochemical laws, and physiological and environmental conditions. To causally entail, and thus to explain the blackness of ravens, one must also cite the basing generalization "All normal ravens have *P*", where *P* stands for the appropriate physiological properties (ibid, pp. 228–229). Basing generalizations can be physically contingent, physically necessary or perhaps metaphysically necessary, but one thing to note is that they need not be causal generalizations. Hence non-causal factors can play a role in the explanation, a theme I will reprise below. A basing pattern of phenomena corresponding to a basing generalization play an explanatory function in a manner like initial conditions in event explanation. A major difference between basing patterns and initial conditions is that since the former concern regularity explanation, they include not just actual but also counterfactual states of affairs (p. 235). For basing generalizations to play an explanatory function requires that they are subject to counterfactual constraints, the details of which I omit here (but see Strevens 2008 Sect. 7.3).

no idealizations. The canonical model implies the same thing as the idealized model but does so by remaining silent about the causal irrelevances. In other words, it simply leaves out the irrelevant details. Now Strevens' account is an *ontological* conception of explanation in the sense that difference-makers are those objective casual facts we draw upon in providing explanations. These causal facts are what constitute the "setup" of our causal models. A canonical model is just such a collection of causal facts. However, an *idealized* model is not merely a collection of causal facts because it contains falsely distorted causal irrelevances as well as causal facts or difference-makers.

13.3 Idealization, Pericyclic Reactions, and Molecular Orbitals

Prima facie, Strevens' account of the explanatory function of idealization seems amenable to quantum chemistry. Take for example molecular orbital approaches to the explanation of pericyclic reactions. These reactions take place in a single kinetic step via a stable transition state in a closed circle of bonds. Pericyclic reactions are of great significance to synthetic chemistry because they include cycloaddition reactions including the Diels-Alder reaction and sigmatropic rearrangements like the Cope rearrangement. Both quantitative and qualitative quantum chemical models of these reactions have been developed by applying molecular orbital theory. Fukui's "frontier" molecular orbital approach allows one to use perturbation theory to calculate the activation energies of two molecules when the reactants do not differ greatly in their structure from the transition state. Since the perturbation expression is too difficult to solve given the complexity of the systems of interest to chemists, all terms are neglected except for the one with the smallest denominator: the highest occupied molecular orbital (HOMO) of one reactant and lowest unoccupied molecular orbital (LUMO) interaction of the other (i.e., the "frontier" molecular orbitals). The frontier orbital idealization therefore reduces a complicated perturbation expression to a single term (Dewar 1989, pp. 302–303). Woodward and Hoffmann famously developed the qualitative sibling of the frontier orbital approach by proposing that the symmetry of the molecular orbital wave functions corresponding to the bonds broken and formed during a reaction determines the stereochemical course of the reaction (Hoffmann and Woodward 1968). When the symmetry of the molecular orbital wave functions is conserved, the reaction is "allowed" in the sense that it requires a relatively small input of energy for the reaction to proceed. And when symmetry is not conserved, greater energy is required for the photochemical promotion of electrons to higher energy (non-bonding) molecular orbitals.

Both frontier molecular orbital and orbital symmetry approaches represent a significant divergence from classical chemical models of pericyclic reactions (the term "pericyclic reaction" belongs to Woodward and Hoffmann). One of the

problems that confronted chemists from the early twentieth century until the mid-1960s concerned the failure of these reactions to obey classical mechanistic criteria because the reactions demanded a way to conceive of a reaction taking place without the bonds being "free" as reactants changed to products via the transition state. This excluded the idea that bond breaking and formation could occur via either of the classical mechanistic options open to theoretical chemists: ionic and radical processes. By using molecular orbital theory, symmetry conservation could be conceived in an analogous fashion to the quantum chemical explanation of the resonance stabilization of benzene. This represented the introduction of an entirely new class of organic reaction, generalized to what chemists had formerly thought to be either unrelated reactions (say, the Diels-Alder reaction and the Cope rearrangement), or merely related by analogy (such as the Cope and Claisen rearrangements).[3]

Quantitative frontier molecular orbital and qualitative orbital symmetry approaches generate explanations of their explanatory targets by making significant idealizations. They ignore the influence of the sigma bonds that make up the underlying carbon skeleton. They ignore the topology of the molecular orbitals that make *some* contribution to a reaction and are therefore casually salient. Following Strevens, one might regard the former, for example, as idealizations in the sense that they set a parameter to an extreme or default value (essentially zero), and in these respects orbital symmetry models are false. But the crucial point is that these idealizations do not make a difference to the causal dynamics of pericyclic reactions. They merely make explicit the irrelevance of some actual causally salient feature of the system modelled. The difference-makers are the key causal factors of the mechanism – the frontier orbitals – and while the use of idealizations means that they are subject to exceptions, it is at least approximately true that when the symmetry of these molecular orbitals contributing most to a reaction is conserved, there is a preference for the reaction to proceed by an energetically favourable synchronous concerted mechanism.

What counts as a "veridical counterpart" to idealized frontier orbital models and a "canonical model" in chemistry? The former might include low-level computational models in quantum chemistry that attempt to solve complicated perturbation expressions by including more than the frontier orbitals (such as models of perturbation molecular orbital theory), or more generally, computational models that yield more precise results by providing approximate solutions to the Schrödinger equation. As for a canonical model, one can only assume that this is a hypothetical construct because we seem to lack the capacity to model complex systems in chemistry without making idealizations and approximations. But perhaps this is a relatively trivial issue given that there is not much to choose between canonical and idealized models when we attend to the ontological sense of explanation. If we wish to individuate idealized and canonical models, it seems we cannot by attending *only* to the factual content of our models – the difference-makers. Canonical and

[3] See Fisher (2006).

idealized models are equivalent in this respect. So, in the ontological sense of explanation, an idealized explanation is just as good as the canonical explanation. But Strevens is swift to reject the explanatory equivalence of idealized and canonical models.[4] Idealized models are explanatorily deficient because they plumb treacherous waters by getting into the issue of the irrelevance of some causally salient factor. They may be deficient because they make a causal irrelevance explicit without explaining *why* it is irrelevant. To take one of Strevens' central examples of idealization, by ignoring molecular collisions in explaining the ideal gas law one might construct an idealized model that explains the law but does not tell us why molecular collisions are irrelevant to the causal entailment of the explanatory target. Or by assigning an extreme value to a parameter, idealized models falsely imply that a causally salient factor makes no difference at all.[5] So an idealized model can increase explanatory power relative to its veridical counterpart but it is not as good an explanation as a canonical model.

13.4 Intrinsic and Extrinsic Functions of Explanation

An important issue concerns the extent to which Strevens' account succeeds in delivering an account of idealized explanatory models. Where idealized models really come into their own is not in the ontological mode of explanation at all. The crucial difference between canonical and idealized models, and the explanatory virtue of idealization itself, is really appreciated once one shifts attention from the ontological sense of explanation to what Strevens calls the "communicative" or pragmatic sense of explanation. Explanation in the communicative sense is not concerned with the objective explanatory facts but rather the "explanation's means of representation" (op. cit., p. 320). It is in the communicative sense that idealized models are individuated and prove to be "valuable scientific all-rounders" in three ways (ibid, p. 321). First, they highlight causally salient details that are nonetheless irrelevant to the causal entailment of the explanandum, thereby helping us to appreciate those irrelevances by explicitly distorting them. By the conspicuous omission of the bonds forming the underlying carbon skeleton, one is in a sense drawn to explanatorily irrelevant but nonetheless causally salient factors. Second, idealized explanations are simpler than veridical models, and they can also be

[4] According to Strevens, individuating models that explain in the ontological sense must be carried out by attending to not only the setup but also to the "follow-through" – a deduction of the explanatory target from the setup, which "represents the way in which [the difference-makers] make a difference" (ibid, p. 319). By taking the follow-through into account one can individuate canonical and idealized models because the former "contains more objectively explanatory information than the idealized model" (ibid, p. 320).

[5] In other words, it does not mean that the value for the parameter makes no difference; it is just that whatever value it does take it will not make a difference to the occurrence of the explanatory target, or that the value must fall within a certain range (ibid, p. 320).

simpler than canonical models because while the latter are optimized by providing a range of bounded values for a specific parameter, idealized models provide them with a definite value (an extreme default value) and this can make it easier to deduce the explanatory target. This certainly seems true of frontier orbital and orbital symmetry models. Third, idealized models are good predictors because only non-difference-makers are distorted. Frontier orbital and orbital symmetry models are indeed prized as good predictors. In fact, Woodward and Hoffmann's approach is a much prized means to predict the course of chemical reactions (Brush 1999, p. 286).

But what is the *intrinsic* explanatory function of idealized models? Strevens' "ontology-first" approach implies that while an extra-ontological sense of explanation performs some constructive role in scientific practice, there is nothing "internal" to the kairetic account to motivate the use of idealized models. They perform an extrinsic explanatory function in the communicative or pragmatic sense of explanation, but that is not a part of Strevens' account of explanation as causal difference-making because idealization is the distortion or omission of *non*-difference-makers. As Strevens points out, it is only by drawing on an extrinsic idea of "explanation" that one can deliver a positive role for idealized explanations: we need "a novel proposal about the meaning and purpose of idealization that is independent of the kairetic account" (op. cit., p. 315). The novel proposal is presumably that unlike other accounts of explanation, in particular pragmatist accounts that (Strevens argues) provide little in terms of a positive cognitive function for idealization, idealizations certainly raise awareness of causal irrelevances. But idealized models are still explanatorily second best because the idealizations themselves do not contribute to the casual entailment of the explanandum, nor do they tell us why certain causally salient factors are explanatorily irrelevant. As for the other proposed virtues of idealized models, emphasising their simplicity and predictive virtues doesn't seem to get us very far. Pragmatists would presumably accept this. If idealizations merely make non-difference-makers explicit in the communicative sense of explanation, then they are explanatorily redundant in the ontological sense of explanation. The result is a deflationary account of idealized explanation because idealization is not connected to causal difference-making.

It is entirely legitimate for Strevens to regard idealizations as explanatory in an extrinsic sense given his commitment to the ontological sense of explanation. This sense of explanation would seem to pose problems from significant parts of the explanatory content of chemistry. By assigning a zero value to the contribution of sigma bonds and thus to regard them as irrelevant to the causal entailment of the explanatory target is one thing. But it should be readily apparent that a considerable difficulty remains when one attempts to cash out the explanatory function of *any* orbitals (atomic or molecular; and concerning the latter, "frontier" or otherwise). The orbital concept is predicated on the semi-classical electron configuration model. The orbital idealization has lost it physical significance except in the case of one-electron systems (like the hydrogen atom) because individual electrons in many electron atoms are not in stationary states; only the atom as a whole could be said to be in such a state (Scerri 2001, S79). Atomic orbitals are essentially

mathematical devices: "basis sets, or a form of coordinate system, with which the wave function of an atom, ion, or molecule can be expanded mathematically to any degree of accuracy dictated by the available computational power" (ibid). I take it that most chemists would consider the models constructed on the basis of atomic orbitals to be highly idealized and of approximate nature, but not causal facts per se. They are not to be taken literally in all respects. Indeed it is difficult to resist the idea that the term "orbital" is non-referential and hence defending an ontological commitment to "chemists' orbitals" is a challenging task.[6]

Similar concerns apply to molecular orbitals. One constructs molecular orbitals and populates them with electrons is a manner analogous to an individual atom by adopting the linear combination of atomic orbitals (LCAO) approximation. While this might lend the impression that molecular orbitals are merely an extension of atomic orbitals, they are conceptually distinct. An atomic orbital is a description of the state of motion of an electron subject to the influence of a single nucleus plus other electrons. But molecular orbitals describe electron motions in the field of two or more nuclei plus the other electrons and the use of the LCAO method is merely a matter of mathematical convenience (Gavroglu and Simoes 2012, p. 83). The delocalized character of molecular orbitals is conceptually quite distinct from the idea of atomic orbitals, and Mulliken – one of the originators of the molecular orbital approach – was at pains to distinguish his "conceptual scheme" from the methods employed to compute them (ibid, pp. 84–85).

Although conceptually distinct, molecular orbitals are methodologically underwritten by the idea of electron configurations and depend on atomic orbitals for their veracity. And the use of molecular orbitals in the study of organic reactions requires significant idealization. Perhaps they could be treated as idealizations which might have been intended to be taken literally, but it turns out that they are not causal difference-makers after all. They would then be what Strevens calls a "preidealization" (op. cit., p. 300). They are simply errors, but only mild ones because they do not damage our explanations as much as an error one might make by misrepresenting a genuine difference-maker. An example of what Strevens has in mind is Newton's explanation of Kepler's laws. Attributing a force of gravity to the explanation of Kepler's laws was meant to be taken literally, but in an age of relativistic physics we know that force is an addition that does not make a difference to the explanatory target. We no longer take Newton's explanation of Kepler's laws literally, although most would agree that it still has some explanatory power (ibid pp. 327–329).

The extent to which preidealizations have explanatory power is again an issue that lies outside of the kairetic account proper because it turns out that they do not misrepresent causal difference-makers but they might enjoy a potential extrinsic explanatory function in the communicative mode of explanation. But molecular orbitals are different. They are presumably not intended to be taken literally, but *are*

[6] This would require a defense of the ontological autonomy of chemistry. For an example of such a defense, see Lombardi and Lambarca (2005).

conceived as fulfilling a cognitive explanatory function which goes beyond merely raising awareness of some actual but non-difference-making property. In other words, they are intended to be taken as making a difference to their explanatory targets. The explanatory strategy appears to be one of *idealizing a difference-maker*. Idealized difference-makers are illegitimate in the kairetic account because they would distort the causal facts and undermine the causal entailment of the explanatory target.

So, there are idealizations in chemistry that either lie beyond the reach of the kairetic account because they idealize difference-makers, or alternatively they simply do not explain. Within the kairetic account, as an ontological conception of explanation, the latter option would be the correct strategy and is also preferable in virtue of the strong emphasis Strevens places on *depth* of scientific understanding achieved through standalone explanations at the fundamental physical level.

13.5 Depth, Causal Ecumenism, and Modularization

The drive towards standalone explanations – cohesive explanations consisting of a complete set of difference-makers (picked out by the kairetic procedure) that causally entail the production of the explanatory target – is to provide depth to our scientific understanding of nature. Strevens' favoured sense of depth resides "in models that account for a phenomenon by picking out a causal structure that is at the same time very abstract and very physical"; causal models that pick out facts about causal influence at the fundamental physical level *and* are very abstract or general (ibid, p. 137).

But not all models are deep along both the axis of physical depth and generality. This "shallow" sense of depth concerns a kind of abstraction or generality achieved by black-boxing. Black-boxes can stand in for a mechanism within what Strevens call the explanatory framework. The explanatory framework is essentially a specification of the explanatory context, which includes causal factors one must assume in order to provide an explanation. For example, to explain the cause of a fire one must take it as given that oxygen is present. But the presence of oxygen is not taken as a difference-maker and hence does not contribute to the causal entailment of the explanatory target. Black boxes can stand in for a known mechanism in the explanatory framework as a matter of mere convenience and lack explanatory power because they are framework relative. Although they may causally entail their targets in a particular explanatory context and so technically stand alone, Strevens argues we should seek unqualified explanations excised of their connection to a particular framework.[7] Only deep standalone explanations are

[7] Outside the context of an explanatory framework, Strevens argues that black box explanations do not causally entail their targets and are incohesive (multiply-realizable – realised by diverse causal mechanisms) (ibid, p. 153).

framework independent and deep along both the axes of generality and physical basis (ibid, pp. 152–154).

Black boxed explanations are pertinent to chemistry because one might interpret an explanation in chemistry as black boxed and standing alone only in virtue of its framework relative conceptual basis – only in virtue of the conceptual and linguistic resources of chemistry. While such "autonomous" chemical explanations may causally entail their explanatory targets, they do not do so independently of their framework because they merely substitute for the "real" mechanism spelled out at the fundamental physical level. Strevens' ontological commitments are also illustrated by his treatment of causal laws in the special sciences. For example, explanations in biology and chemistry are offered without citing physical covering laws. But the shallowness of depth, Strevens insists, is only "apparent" because a chemical causal law is "identical to the components of the causal model that explains it" – identical to the "underlying physical mechanism" (assuming appropriate background conditions and correspondence rules linking low with high level statements or properties) except for parts that might be merely not "spelled out", or made "fully explicit" (ibid, p. 130). He argues that all causal influence is fundamental (low-level) physical causal influence. Explanations stand alone when high-level causal laws are abstractions, purged of the irrelevant low-level (physical) causal details such that they contain only those properties and processes relevant to the entailment of the regularity or event to be explained.

This is grist to Strevens' ontological mill. His account of deep standalone explanation is a commitment to physicalism based on "empirical fact" not a priori argument (ibid, p. 82). Strevens' reductionism is a clearly an issue that might meet with resistance, but it is not the purpose of this contribution to engage with reduction save for its connection to idealization and explanation. What's missing in Strevens account is a clear sense in which we could apply Strevens' ideas to an actual case of explanation in chemistry because the same problem concerning the explanatory function of idealization in chemistry arises again. If one assumes a physical basis for all causal influence and one cannot derive the properties and processes attributed to chemistry, then the physical extension of at least some terms of causal explanatory importance to chemistry, like "molecular shape", "bond", "orbital", etc., seems to be an empty set. If one were to conclude that models employing such terms are explanatory in the communicative sense only, then even this option seems to be blocked. Idealization is the distortion of actual but causally irrelevant factors whose cognitive function is to at least raise awareness of those factors that play no role in the causal entailment of the explanatory target. On a reductionist view, since the physical extension of at least some chemical terms is an empty set, it follows that the conceptual resources of chemistry often fail pick out not only causal facts about the world but also communicatively significant but causally irrelevant aspects of their target systems. In other words it turns out that on the kairetic account, much of the causal resources of chemistry are neither difference-makers nor non-difference-makers. So, it seems that chemistry does not explain in either the ontological or communicative senses of explanation as Strevens construes them.

Strevens' commitment to physicalism and a deflationary, externalist idea of the role of idealization in explanation appears to be highly restrictive. It rules out much scientific practice, at least so far as explanation in chemistry goes. Those of us interested in defending a more inflationary view of explanation in chemistry need an alternative strategy. Even if one is not committed to physicalism, one must admit that there are significant problems confronting an account of explanatory idealization given that idealizations will misrepresent the causal production of phenomena. But while Strevens account is restrictive, in another sense it is surprisingly permissive. A result of this permissiveness is that even if idealization in chemistry is the distortion of causal difference-makers – a central claim of this chapter – this does not entail giving up on the kairetic criterion of explanatory relevance.

Strevens' adopts a "two-factor" approach to causal explanation. His aim is to distinguish the metaphysics of causation and a criterion of explanatory relevance. He is ecumenical in his attitude to the metaphysics of causation and defends the idea that identifying the causal relation – causal influence – is a necessary but not a sufficient condition for explanation. A *one*-factor view is the idea that the causal influence is sufficient for explanation. According to Strevens, the disadvantages with the one-factor view are many. For one thing, it lets in too much. It seems to commit us to a view of explanation in which *all* casually salient factors – all the actual causal influences – are explanatorily relevant. But explanation is selective. So, while one factor of explanation is the causal relation itself, the other factor is a non-causal criterion of explanatory relevance. And that is what the kairetic criterion provides. It is a selection rule driven by the kairetic procedure of optimization. A high-level relation of causal influence – "*c* is a cause of *e*" – is not an assertion of causal influence, but rather an assertion of an explanatory relation between two events, namely *c* and *e*. The explanatory relation is both a "low-level causal influence relation and a high-level explanatory relevance relation" (ibid, p. 51). Combining a high-level explanatory relation with a low-level (i.e. physical) causal influence relation, "gives you both the truth conditions for causal claims and an account of the high-level *is a cause of* relation, now understood not as a purely causal relation but as the causal-explanatory relation, the relation that an event must bear to another event in order to participate as a cause in its explanation" (ibid).

According to the two-factor approach, in explaining a phenomenon we select just those and only those causal facts that make a difference to the causal production of the explanatory target, underwritten by a metaphysical dependency relation of causal influence while remaining silent as the metaphysics of causation itself. But note that Strevens account is also a *modular* theory of explanation. One doesn't just select for explanatory relevance; one also selects a "domain of dependence relations that must be appreciated in order to understand the phenomenon to be explained" (ibid, p. 5). If the domain of dependence is a causal, then we have a causal explanation. Strevens himself points out that the domain of dependence need not be causal. Mathematical dependence is one candidate of non-causal dependence of interest to philosophers of scientific explanation (ibid, p. 180). It sounds like causal influence isn't even a necessary condition for explanation, and Strevens himself suggests a "partial revision" of his account such that "the difference-making criterion takes as its raw material any dependence relation of the 'making

it so' variety, including but not limited to causal influence" (ibid). The "making it so" relation (the meaning of which is up to the reader to ascertain) and the entailment relation (or some cognate) is all that is required. On one hand, Strevens' two-factor approach permits an ecumenical stance with respect to the metaphysics of causation by not getting into the issue of the relation of causal influence itself. On the other hand, modularization permits Strevens to claim that one could detach the two factors: causal influence and the kairetic criterion of explanatory relevance (ibid, 179). Is Strevens more committed to the difference-making criterion than the relation of causal influence itself? Surely not. But while Strevens' two-factor approach entails ecumenism regarding the metaphysics of causation, his modularism makes it all the easier to concede that not all explanation is causal explanation. Are there any other contenders?

13.6 Symmetry and Non-causal Difference-Making

The positive suggestion to be sketched here is that there are *non*-causal dependencies in quantum chemistry – dependencies not captured by the relation of causal influence and so independent of an ontology of causes –, and this can address the problem with explanatory idealizations construed as the misrepresentation of *causal* processes while retaining Strevens' difference-making criterion of explanatory relevance. At the very least, one can point to the explanatory power of an explanation tied to a domain of non-causal influence even if models idealize the causal story.

Let us return to the difficulties described above concerning the situation that confronted chemists when they attempted to provide classical causal-mechanical explanations of cycloaddition reactions and intramolecular rearrangements. These difficulties were overcome once Fukui, and Woodward and Hoffmann began to apply the molecular orbital theory to the study of organic reactions. Recall that Woodward and Hoffmann recognized that the relevant class of reactions could be described as taking place in a closed circle of bonds wherein bond breaking and formation took place simultaneously in a single kinetic step. Woodward and Hoffmann provided a much sought after causal mechanical explanation of a group of reactions of crucial synthetic importance. One shouldn't underestimate the importance of the importance of framework relative causal mechanical explanations to chemists at that time (they still do) (Fisher 2006). Shortly before the introduction of the Woodward-Hoffmann approach, physical organic chemists Doering and Roth (1962, p. 67) jokingly referred to "no mechanism reactions", thus highlighting the inability of classical mechanistic criteria to explain what would come to be called pericyclic reactions. While the "no mechanism" designation was dropped after Woodward and Hoffmann published their ideas in a series of papers in the mid-1960s, it is also crucial to recognise that Woodward and Hoffmann were engaged in project that went beyond mere causal explanation. For one thing, their selection rules for pericyclic reactions – the Woodward-Hoffmann rules – highlighted the considerable value that chemists placed in models

capable of predicting the stereochemical course of organic reactions. But there was also a crucial development in the kind of explanations that came with those rules. Woodward and Hoffmann's approach provided the means to go beyond causal explanation. In fact, one did not provide an explanation of pericyclic reactions without doing so.

Woodward and Hoffmann's approach was an essentially "qualitative" application of molecular orbital theory to the study of organic reactions. Care is required in the interpretation of the term "qualitative". It does not mean an absence of mathematics. Drawing on Hoffmann's own sense of the term, Weisberg (2004, p. 1071) argues that "qualitative" expresses the extent of approximations and idealizations employed in modelling rather than a lack of numbers. This is important because Woodward and Hoffmann's crucial insight was that the relative phase *symmetries* of the molecular orbitals representing the bonds broken and formed during a reaction *make a difference* to whether a reaction is thermally allowed or forbidden. In order to explain why a given pericyclic reaction takes place in a single kinetic step and bond breaking and formation occurs simultaneously, one idealizes by, for example, ruling out the explanatory relevance of the bonds comprising the carbon skeleton, and then applies the molecular orbital theory to the idealized causal model. This is a "bottom-up" (driven by experiment) as much as a "top-down" (theory-driven) process. It is not that one begins with the domain of physical causal influence and then one distils a standalone explanation shorn of causal irrelevances. Rather, one begins with framework relative, black boxed causal mechanical explanations which are idealized in the sense that they distort the causal story. While this might sound as if we have moved beyond the bounds of veridical explanation according to the kiaretic account, one must look at the aim of the modelling strategy employed in the explanation of pericyclic reactions. One moves from a causal-mechanical representation of a reaction to the construction of molecular orbitals, classifying their symmetry properties, and then following the dynamics of the reaction through in the model, as it were, by correlating energy levels of like symmetry.

The procedure is effectively a matter of explanatory model construction that begins with a simple idealized model of the geometry of approach of the reagents relative to a given plane or planes of symmetry. One then considers the symmetry of the orbitals contributing most to the reaction (the "frontier" molecular orbitals) under groups of transformations such as reflection or rotation with respective those planes of symmetry. In order to determine the symmetry of the molecular orbitals, one solves the Schrödinger equation via the linear combination of atomic orbitals (LCAO) approximation, which replaces a many-electron wave function with a molecular orbital consisting of electron pairs:

$$\psi = c_1\phi_1 + c_2\phi_2$$

where ψ is the molecular orbital wave function, ϕ_1 and ϕ_2 the wave functions of the atomic orbitals, and c_1 and c_2 the coefficients expressing the mutual contributions of

atomic orbital to the molecular orbital wave function. Two atomic orbitals generate two molecular orbitals, one lower in energy than either ϕ_1 or ϕ_2 – the bonding molecular orbital and one higher in energy – the antibonding molecular orbital. Replacing a many electron wave function by molecular orbitals consisting of electron pairs is a significant idealization, but nonetheless a crucial part of the process of abstraction because it allows one to determine explanatorily relevant factors by permitting the classification of the relative phase-symmetries of the molecular orbitals contributing most to the reaction and hence the relative energies of those orbitals. The signs of the coefficients c_1 and c_2 in a bonding molecular orbital are either both positive or both negative, which means that it is an in-phase, bonding combination of the atomic orbitals. The coefficients of an antibonding molecular orbital are of opposite sign, i.e., out-of-phase.

By developing this computational model, one can construct the molecular orbitals corresponding to the bonds that break and form in the reaction and classify those molecular orbitals according to their symmetry properties under reflection in at least one plane. Finally, in order to explain why a reaction occurred in the way that it did, and to predict the stereochemical course of a reaction, one constructs a qualitative *orbital correlation model* with the approximate energy levels of the reactants on one side, those of the product on the other, and the intermediate region representing the reaction transition state. By correlating the molecular orbitals of bonds broken and formed during a reaction according to the relative phase symmetries of the molecular orbital wave functions, one can determine whether a given reaction is energetically favourable and allowed (symmetry is conserved) or whether it is energetically unfavourable or "forbidden" (symmetry is broken) because it requires the photochemical promotion of electrons to higher energy antibonding molecular orbitals.

Symmetry is a domain of non-casual dependence that underwrites the kairetic criterion of difference-making in the quantum chemical explanation of pericyclic reactions. The orbital correlation model contains those factors – the symmetry of the molecular orbitals – that make a difference to the explanatory target. It is used to explain why a reaction occurs in the way that it did occur, or indeed why it did not occur. By citing the symmetry of molecular orbitals as difference-makers, the invariance of the symmetry properties of molecular orbitals (the conservation of orbital symmetry) explains why a particular reaction is allowed and, when symmetry is broken, why it is forbidden. It should be noted that symmetry is *not* simply a matter of mathematical explanation wherein the explanandum represents some domain of abstract mathematical relations. Explanatory relevance is matter of determining those mathematical structures that make a difference to, and hence entail (though not *causally* entail), their explanatory targets – regularities and concrete events in organic chemistry. What we end up with *are* idealized explanatory models. But the shift of the domain of dependence "away" from the causal story results in a model that is not explanatorily illegitimate. The idea that orbital symmetry is a difference-maker is embodied in Woodward and Hoffmann's famous *selection rules* – the Woodward-Hoffmann rules – providing synthetic

chemists with models of considerable predictive power.[8] Although there are exceptions to the Woodward-Hoffmann rules, orbital symmetry models have considerable explanatory power relative to more detailed and accurate lower-level veridical models of computational quantum chemistry. In fact, the orbital symmetry control of organic reactions has received demonstrable theoretical support from lower-level ab initio computations (Houk et al. 1995).

Idealization plays a crucial in the construction of explanatory models because it is an ineliminable part of the procedure used to classify the symmetries of molecular orbitals. The use of the LCAO method demonstrates the interconnectedness of idealization and difference-making. It is by adopting this method that one can extract the crucial explanatorily relevant details in spite of the serious limitations of that method. This might be an illegitimate move if one were attempting a *causal* explanation along the lines of Strevens' approach. But unlike Strevens' account, the procedure of abstraction does not begin with physical causal influence. At the very least, one can think of it as a methodological hedge: in order to distil those explanatorily relevant factors from the kinds of systems of interest to chemist, one is going to have to get a bit dirty. The ontological cost of the idealizations and approximations can be offset since it is a step *towards* a lower level explanation in terms of the difference-making *state* symmetries of the target system even if one is thereby undermining the causal story itself. The process simply goes beyond the idea of a kairetic procedure applied to causal systems because one is attempting to distil from an idealized putative causal representation of a chemical reaction another model containing those properties of states that make a non-causal difference to the explanatory target. Building up molecular orbitals and then populating them with electrons, which if taken at face value is highly approximate and idealized since the use of the LCAO method is underwritten by the assumption of electron configurations, we ultimately leave the causal story behind. In this case, idealization is a crucial feature of the procedure for determining explanatory relevance. Idealization therefore has a more intrinsically positive function in the sense that it is not just limited to a communicative sense of explanation constrained to non-difference-makers. The idea of non-casual difference-making can be more flexible and inclusive. One can admit of an intrinsically constructive explanatory role for idealizations in the sense that they are an ineliminable feature of the procedure for determining those states of a system that make a difference to their explanatory targets.

[8] For example, a thermally allowed cycloaddition is the 4 + 2 cycloaddition of ethene and butadiene, i.e. the Diels-Alder reaction. The corresponding selection rule is: $m + n = 4q + 2$, where m and n are numbers of pi-electrons, q is an integer 0, 1, 2… (Hoffmann and Woodward 1968, p. 827).

13.7 Conclusion

One cannot ignore the idealization of causal difference-makers in chemistry. In spite of the fact that causal processes are often misrepresented in chemistry, some of the most important approaches to modelling the stereochemical course of organic reactions posit non-causal dependencies and cite non-causal difference-makers that entail their explanatory targets. If there are non-casual dependencies, one might detach causal influence and the kairetic procedure of for determining explanatory relevance. The result is that the symmetry control of organic reactions is a case of non-causal explanation in chemistry which is nonetheless compatible with the kairetic criterion of explanatory relevance, modified in that it is no longer tied to the domain of physical causal influence.

Of course, what has been provided in this chapter is only a sketch. Much more could be said about the connection between symmetry and explanation. But it should be noted that this is an area that has received relatively little attention in the philosophical literature on the foundations of physics, let alone the philosophy of chemistry. Brading and Castellani (2007, 2013) provide some useful suggestions concerning the relationship between symmetry and explanation in physics, as well as the ontological and epistemological status of symmetries. The latter issue is of crucial importance to explanation too, for it will impact on what conception of explanation – ontological or epistemological – one defends. As far as this author can determine, however, no connection between symmetry and explanation as difference-making has been made. The explanatory function of orbital symmetry might be spelled out further as an application of symmetry arguments in chemistry. An intriguing possibility (restricted to deterministic systems and admittedly subject to interpretational difficulties and profound disagreements as to its significance) is that there is a relationship between Woodward and Hoffmann's essential idea of the symmetry control of pericyclic reactions and "Curie's principle". This principle arises from Pierre Curie's interest in the connection between the physical properties of crystals (such as their thermal, magnetic and electric properties) and symmetry; in particular which physical phenomena are allowed to happen given the symmetry properties of a physical medium (Brading and Castellani 2013). Curie's principle might be simply expressed as "The symmetry of a cause is always preserved in its effects" (Ismael 1997, 167), or "When certain causes produce certain effects, the symmetry elements of the causes must be preserved in the effects" (Brading and Castellani 2007).[9] As is well known, Curie's principle is undermined by spontaneous symmetry breaking. But there might be enough of interest remaining in the "principle" to explore its relationship to orbital symmetry, and that the chemical properties of substances might be related to the symmetry properties of molecular structure and dynamics. That might offer a means to further explore the relationship between symmetry and causation in chemistry.

[9] An influential interpretation of Curie's principle is provided by Chalmers (1970). See also Earman (2004).

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Chapter 14
Investigating the Meaning of the Ceteris Paribus Clause in Chemistry

Jean-Pierre Noël Llored

14.1 Introduction

Ceteris paribus is a Latin phrase, translated as "holding other things constant" and is usually rendered in English as "all other things being equal." This condition is essential for the predictive purpose of any scientific inquiry and remains, explicitly or not, a prerequisite for the validity of most inferences by comparison between cases. Scientists first assume that one or more factors are fixed with the view to analyzing the influence of another factor "in isolation." This isolation can be temporal if the factors fixed under the *ceteris paribus* condition actually change slowly *relative to* other influences. In this situation, they are considered to be practically constant during the experiment. Scientists can also refer to a causal isolation if the factors frozen under the *ceteris paribus* condition are not significantly affected by the process under study. Following this line of enquiry, not only do experimentalists have to decide if a factor is negligible or not, but they also have to define a relevant domain of study – macroscopic, mesoscopic, microscopic or nanoscopic, and ensure that the phenomenon remains stable enough in order to investigate the behavior of the system by the instrumentation at hands. In brief, scientists gradually identify and stabilize the context from which a comparison between cases paves the way for relevant inferences within a problem-solving process.

Scientific conclusions must abide by this condition of comparison. In this respect, the *ceteris paribus* condition is normative and is closely related to the possibility of acceptable inferences from the special circumstances actually

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present within a particular scientific survey. Drawing on Wittgenstein's terminology (1974), we could claim that the *ceteris paribus* clause turns out to be a "hinge" around which most inference strategies revolve. If this "hinge clause" seems to be a condition of possibility of making inferences, is its application universal or local?

To address this problem, we shall first characterize the activities of chemists. If the "properties" of bodies are, even partly, constituted by the mode of access, for example by an instrument, within a chemical transformation, it seems that the sentence "all other things being equal" should be understood in a specific way. What sometimes appears to be a universal clause or metaprinciple turns out to be a local hinge that a "distributed epistemology" (Bachelard 1940), enables us to clarify and explore further.

It is worth noting that chemists tend to consider chemicals to be active bodies endowed with capacities of action in order to explain the consequences of their introduction into a complex of material stuffs. Chemists always deal with and act upon heterogeneous and active "matters." This way of looking at chemical reactions is at odds with the search for a coherent understanding of passive matter *in general*. In the framework of both context-sensitive and active bodies, *a bearer of an attribute does not necessarily have an "identity" independent of that attribute throughout the transformation involved*. Furthermore, if many parameters such as the chemical composition of a mixture, the surface of a chromatographic column, the polarity and the flow of the solvent, and the temperature, to quote but a few factors, are bound to change during a chromatographic analysis, another question arises: How is it possible to control for all of the independent variables other than the one under study, so that the effect of a *single* independent variable on the dependent variables can be isolated?

We do not propose to set out a ready-to-use philosophical analysis from the outset but, on the contrary, to identify what a philosophical enquiry should integrate into its premises in order to investigate the meaning of the *ceteris paribus* clause in chemistry.

We shall explore the domain of analytical chemistry, and especially that of quality control. This will allow us to emphasize that the application of the *ceteris paribus* clause implies that we adapt our understanding of what is "stabilized" within such practices. Both the "object" on which the clause rests and the meaning of the clause itself change together in the context of chemistry. We shall demonstrate that what is stabilized in a chemical preparation is the response of the whole complex that holds the apparatus, the chemical bodies and the microstructures of interest, the methods being used, and the surroundings solvents or other extrinsic chemical bodies and the gravitational and electromagnetic background. The inference is thus about this complex and certainly not about chemicals or single factors in "isolation."

14.2 Prerequisites for Chemical Activities

14.2.1 Operations, Relations, and Relata

A chemical body is defined by means of the attributes that it can display in a precise context and also by means of the operations involved to individuate it. Let us just illustrate this with Peirce's definition of lithium:

> If you look into a textbook of chemistry for a definition of *lithium*, you may be told that it is that element whose atomic weight is 7 very nearly. But if the author has a more logical mind he will tell you that if you search among minerals that are vitreous, translucent, gray or white, very hard, brittle, and insoluble, for one which imparts a crimson tinge to an unluminous flame, this mineral being triturated with lime or witherite rats-bane, and then fused, can be partly dissolved in muriatic acid; and if this solution be evaporated, and the residue be extracted with sulphuric acid, and duly purified, it can be converted by ordinary methods into a chloride, which being obtained in the solid state, fused, and electrolyzed with half a dozen powerful cells, will yield a globule of a pinkish silvery metal that will float on gasolene; [then] the material of *that* is a specimen of lithium. (Perice, 1931–1958, CP 2.330)[1]

Peirce confidently endorses the idea that lithium can be defined as a set of instructions aimed at permitting not only the identification but also the production of a specimen of lithium. This definition is clearly provisional and open-ended so that the word 'lithium' will acquire new meanings as we learn more about the thing or stuff to which it refers. For Peirce reality appears to us under the form of a continuum within which there are no absolute individuals (Peirce, CP 6.170). The *indeterminacy* of operationally defined individuals such as specimens of lithium should be related, according to Peirce, to *a principle of contextuality*: Any discourse about an object cannot exhaust the potentially infinite, determinations of that object. Peirce remarked: 'The peculiarity of this definition is that it tells you what the word *lithium* denotes by prescribing what you are to *do* in order to gain a perceptive acquaintance with the object of the word' (Peirce, CP 2.330).

Operations and instruments were essential parts of the definition of substances in eighteenth-century chemistry. The French chemist and apothecary, Guillaume François Rouelle, asserted that

> [c]hemistry is a physical art which, by means of certain operations and instruments, teaches us to separate the various substances which enter into the composition of bodies, and to recombine these again, either to reproduce the former bodies, or to form new ones from them. (Eklund 1975, p. 2)

In Venel's description of reactions in his "Table des rapports" the relational character of the phenomena is clearly presented.

> One applies mercury to a silver dissolution in nitrous acid; this substance having more relation with this acid, than this acid has with silver, it unites to it and precipitates silver. If one decants the liquor one will have separated silver, and on the other side mercury dissolution in nitrous acid, if one adds a lead blade to this mercury dissolution, lead has

[1] Peirce's use of italics.

> more relation with nitrous acid than mercury, it unites it and precipitates mercury. If one decants it the precipitated mercury remains on one side and on the other side a lead dissolution in nitrous acid; if one adds a copper blade to this dissolution, copper has more relation with nitrous acid and unites to it, lead will be precipitated too and there remains a copper dissolution in nitrous acid; if one adds iron copper is precipitated, if one separates as must always be done, one will have the iron dissolution. (Lehman 2010, p. 21)

At this period, the word chemical "operation" was used to mean what we currently call a chemical "reaction" (Holmes 1996). Analogy was the main guide followed by chemists in order to construe networks of independencies by means of chemical operations. According to George Urbain:

> [e]ach body being a collection of properties, the reasoning by means of analogy implies that those properties are not independent from one another. If one aims at facing the problem of analogy from a chemical standpoint, she must start querying under what limits those properties are interdependent (cited in Bensaude-Vincent 2008, p. 244, our translation).

Relations allow chemists to define chemical entities and properties, while operations allow them to obtain pure chemical bodies. Those bodies then enter into new reactions and result in new compounds that, once purified, allow chemists to widen and deepen their classification by analogy. The process is open-ended and depends on the modes of access which stabilize a certain group of relations. In the context of scientific practices, *relata* do not exist prior to relations, and relations are not achievable without purified chemical bodies. *Relata* and relations *depend on one another* within an *ordered and evolving network* (Llored and Bitbol 2013).

Let us draw our first conclusion: *The meaning of the ceteris paribus clause in chemistry should be understood within a philosophical framework in which both relation and relata have a role to play* (Requisite 1).

14.2.2 Constituting Chemical Bodies: The Role of the Modes of Access

Emphasizing the constitutive role of operations on the definition of chemical bodies, Ursula Klein says:

> [t]he example of early nineteenth-century organic chemistry demonstrates that chemists' new definition and identification of organic substances was entwined with new ways of material production and individuation of these things. The nineteenth-century culture of organic chemistry material production and individuation, and the instruments, skills and connoisseurship involved in these activities, were as much a part of the constitution of the objects of inquiries as theories, beliefs, social interests, and power. (Klein 2008, p. 42)

In a footnote (p. 42): she adds 'I consider experimental production and individuation of objects to be part of their "constitution".'

The material production and individuation of bodies has enormously expanded in current nanochemistry, solid-state chemistry, and materials science. New instrumentation and chemical devices enable chemists to explore temporal and spatial

scales which have been completely unreachable until now. Chemists have gained an enlarged capacity to synthesize, scrutinize, and modify particle size and distribution, agglomeration state, shape, crystal structure, chemical composition, surface area, surface chemistry, surface charge, porosity, and interfaces.

A "science of individuals or particulars" arises and chemists are now able to generate and study multifarious details at the individual level (Llored 2013). Non-stoichiometric compounds are now legion. Chemists even contrive to combine organic and inorganic ingredients into the same hybrid body; thus, holding together types of chemistry which have always been incompatible hitherto. This example strengthens the above mentioned ideas of the *indeterminacy* and *open-endedness* of what is operationally defined. François Dagognet states: 'We must accept the continuous renewed and inexhaustible richness of what is extended' (Dagognet 1989, p. 166). This diversity is not solely a question of ingredients, quantities, and structure. It also depends on the devices and the instruments involved. As a consequence, it is a question of *contextuality* too. Let us take the example of the synthesis of a solid sample of $CaCO_3$ in order to highlight the role played by the context both in the synthesis and the definition of a chemical body.

Starting from different ingredients, particles will grow to attain different final sizes and morphologies (Aimable et al. 2013). Thus, the end product may appear completely different, depending on whether a reactive material is added all at once or gradually. By adding a small amount of fine material to be precipitated (i.e., seeds), one can better control the apparently chaotic nucleation step. For example, adding calcite seeds allows for the precipitation of pure calcite. On the other hand, without seeds, one obtains a mixture of calcite and vaterite with a larger particle size distribution and various morphologies. The body $CaCO_3$ depends on the process used and on the time employed. This body is furthermore distributed or size-dispersed in the sense that the sample does not contain a single body $CaCO_3$ but, on the contrary, encompasses many similar bodies $CaCO_3$ which differ in size. *Neither the device nor the history of the chemical reaction can be eliminated from the final result. Operations are thus part of the definition of the "nanobody" under study.*

The mode of access cannot be eliminated from the final product insofar as it contributes to the determination of the whole body and its correlative parts and structure. The structure of the crystals may also differ if the chemical device changes. It can even differ within the same particular chemical device, depending on the size of the crystals, which itself depends on the environment. *In a nutshell, the internal arrangement can be grain-size sensitive*: *The concept of structure thus sometimes becomes*, *at least partly*, *extrinsic*!

Accordingly, chemists have to hold the composition, the global and internal structures, the parts of the body, the whole body itself, the environment, and the device together within the same coherent explanation. If a chemical body is thus tied to *praxis*, it is not a definite something or mere substrate that endures through time. Instead, it is at all times fully realized as just what it appears to be, and at the same time it never stays the same as it becomes transformed in processes of making, remaking, and learning to make. As an indefinite "something out there"

the chemical body enters into a series of interactions that produce determinate things that are characterized by their consistence and transformability, their performance, and their functionality (Nordmann 2013). In the context of chemistry, the dichotomy of essences and accidents thus collapses.

Let us draw our second conclusion: *The meaning of the ceteris paribus clause in chemistry should be understood within a philosophical framework in which the modes of access do not 'reveal' pre-existing chemicals but, on the contrary, actively take part in their very constitution* (Requisite 2). This constitutive role thus permits limited inferences on how to deal with what is or said to be displayed by the chemical experiment under consideration. In this respect, a philosophical investigation of the issue at stake should address the possibility for the internal structure of a body to depend both on the context and the size of that body. The integration of the relational dimension of what is usually considered to be intrinsic is a starting point to reflect upon what changes when all other factors remain equal and what the words "sameness" and "isolation" may mean in the context of chemistry. To do so, we should not leave the materials aside and just draw our attention to the mode of access only, but rather place the greatest emphasis on the interactions between the two.

Keeping these two requirements in mind, we can investigate the meaning of the *ceteris paribus* clause in chemistry, if we also remember that, in such a context, *there is no reduction of a level of organization by another but codependence between them. Chemists hold the whole, the parts, and the surroundings together* (Llored 2012). To do so, we should follow Rom Harré's recommendation to avoid two mereological fallacies (Harré and Llored 2013):

1. a 'semantic fallacy' which consists in applying to a part of a chemical body a predicate that gets its meaning from its use for ascribing an attribute to the whole body from which the part comes.
2. an 'ontological fallacy' which consists in inferring that substantive products of an analytical procedure exercised on a complex body are always parts or constituents of that body.

The identification of these fallacious patterns of reasoning is context relative and they must be applied judiciously. For example a chemical complex has mass and so do its constituents. But a chemical complex may have analgesic effects but its constituent chemical radicals usually do not.

14.3 The Meaning of *Ceteris Paribus* Clauses in Chemistry

Current experimental work shows that sodium hydroxide pellets react more quickly with the carbon dioxide contained in the air than substantial masses of the substance, under the same circumstances. This reaction of 'carbonatation' is mainly linked to the differences in area of the exposed surfaces and to the carbon dioxide

concentration in the air. A part of the hydroxide ions OH^- is replaced by carbonate ions CO_3^{2-} as follows:

$$CO_{2\ \text{gas phase}} + 2\ OH^-_{\text{solution}} \rightarrow CO^{2-}_{3\ \text{solution}} + H_2O_{\text{liquid phase}}$$

This reaction unavoidably implies the decrease of the concentration of the caustic solution over time, which, in turn, distorts chemical quantification during acid-base titrations if it is not taken into account. While maintaining all other conditions the same concentrated sulphuric acid is far more stable than caustic soda when in contact with the air. The context of application and content of the *ceteris paribus* clause thus differ because of the different reactivity of bodies and their degree of stability which, we have shown it, is closely related to the surroundings. The notion of "fixity" and that of "identity" which traditionally enable scientists to make inferences from comparison can easily become problematic. The content of the *ceteris paribus* clause becomes an object of inquiry as soon as one aims to elucidate the meaning of the clause in actual chemical contexts.

In agreement with our previous arguments, *it is impossible to abstract the body from the operative framework in which it is stored or used*. Accordingly, the practice of inserting a *ceteris paribus* clause cannot deal with any particular reaction of the same body in all circumstances but is, by contrast, primarily concerned with what we shall call the couple {bodies-associated milieu}. The associated milieu can be a solvent or a mixture of solvents, a gas vector, a mineral matrix,[2] and so on.

Only one parameter must vary in order to characterize the chemical behavior of this couple in relation to the qualification "all things being equal." In this respect, the use of the clause does not permit any nomological implication in connection with the intrinsic properties of bodies. The conclusion of chemical reasoning is about the couple {chemical bodies-associated milieu} under study. Both relations and *relata* are thus taken into account at the same time. We have called this Requisite 1 above.

We have now to include the instrumentation that enables chemists to quantify their products in our investigation. We cannot consider the mode of access-apparatus-as a transparent window through which to see the world as it would have existed had the mode of access never been constructed and switched on, which we have called Requisite 2 above. Science is the study of 'apparatus/world complexes' (Harré 2004). Humphrey Davy's isolation of sodium in the metallic state by electrolysis of a solution which contains Na^+ cations is an example of such an apparatus/world complex. It is always possible to claim that an apparatus makes actual in the laboratory that which is potential in nature (Wallace 1996; Cartwright 1989). This reasoning is just another way of considering the apparatus as a kind of window on the world. Such windows do not reveal any actual thing but, on the

[2] The term matrix describes the substrate in which the molecules to be characterized and titrated are located (e.g. biological fluid, vegetable matter, etc.).

contrary, would bring potential powers or capacities to light. This type of reasoning, however, ignores the active contribution of the apparatus to the constitution of the bodies. Should the results of experimentation seen in this light be qualified by *ceteris paribus* clauses?

Many changes have occurred during the course of the experimental procedure implying that many factors have unavoidably moved at the same time. Chemicals are reactive, so is, at least, a part of the apparatus. A mixture of chemical bodies is being separated or transformed while, for example, the active area of the working electrode – or that of a catalyst – changes and permanently alters the ensuing process. The quantities of bodies, the composition of the liquid phase, the dynamics of adsorption and desorption at the surface of the electrodes, sometimes the temperature depending on the energy released during the transformation are all factors that can change simultaneously or almost simultaneously. Sure enough, one could easily claim that everything depends on the scale of the factors at play. Local changes can sometimes be subsumed under a global invariant factor. But is it basically just a problem of scale? Choosing a relevant scale is part of a problem of modeling and depends on chemists' purposes and standards for normalization. According to the argument presented here it is, first and foremost, a problem in the method of choosing and preparing a specific apparatus for studying a particular collection of bodies and, correlatively, a problem in preparing the same collection of bodies for developing a useful interaction with the apparatus when an associated milieu of a certain type and a particular device are being used. The central problem is that of *the co-stabilization* of an apparatus with the set of bodies with which it interacts; a problem which includes various acts of modeling as part of the global project.

It is the whole complex composed by the apparatus, the methods carried out for calibrating and using it, the bodies, the associated milieu, and the ancillary devices which should be the starting point of our epistemological enquiry. To investigate the meaning of the *ceteris paribus* clause in chemistry requires an investigation of the conclusions that chemists can relevantly draw from comparisons with reference to the complex {apparatus-methods-bodies-associated milieu-devices}.

Ultra High Pressure Liquid Chromatography-UPLC-is a column chromatography used to separate, identify, and quantify chemical bodies. A set of pumps pushes the mixture, the mobile phase, through the columns which are filled with a packing material, the stationary phase. As the mobile phase is passing through the stationary phase a specific detector shows the retention times of the different molecules. Retention time varies depending on the interactions between the stationary phase, the molecules being analyzed, and the solvent used. The particle size within UPLC columns decreases to less than 2.5 μm requiring a higher pressure in order to push the mixture through the columns. Since both efficiency and optimum flow rate are inversely proportional to particle size, the UPLC system thus increases efficiency and speeds up the flow rate which, in turn, allows for narrower and taller peaks and, eventually, provides a greater resolution (Alan Xu 2013).

A coupling between the UPLC system and a mass spectrometer enables chemists to combine the physical separation capabilities of liquid chromatography with

the mass analysis capabilities of mass spectrometry-MS. The UPLC-MS is a sensitive and selective device which enables chemists to identify unknown compounds or to determine the structure of a compound by observing its fragmentation *afforded by* the apparatus. It is also possible to include UV-VIS or NMR detector into the system in order to achieve a parts/whole analysis which depends on the associated milieu.

Chemists well know that the study by UPLC-SM of a mixture of antibiotics contained in a sample of water varies according to: (i) the original matrix (wastewater, particular place from which sample was taken along the river), (ii) the associated milieu – the mobile phase which is a mixture of polar and non-polar liquid solvents whose respective concentrations are varied depending on the composition of the sample, and (iii) the nature and the quantity of the antibiotics present in the mixture. The results of the study also depend on internal elements related to the apparatus itself: (1) the pressure, (2) the flow rate fluctuations, (3) the chemical nature and characteristics of the separating column-length, porosity, polarity, specific surface, diameter, use of capillary tubes, (4) the temperature along the process, (5) and the type of detectors and their limits of use (Snyder et al. 2010). In addition, both the parameterization and use of this apparatus depend on the choice of a quantitative method, and the determination of attenuation factors in order to ensure that the value of surface of the peaks corresponds to the concentration of the products. Last but not least, chemists must use a wide range of statistical methods and tests so as to shape their quantitative results in the due form before deciding as to whether a result is validated or not.

In the most recent methodologies, an analysis consists of at least three steps: taking the sample, preparing the sample, and carrying out the physicochemical analysis. If many factors change at the same time, at the end of the process, the concentration of the product must nonetheless belong to the confidence interval defined by a particular standard such as the norm ISO 5725.[3] The confidence interval characterizes the confidence or the credibility which can be ascribed to the result of a particular quantitative determination. Confidence intervals consist of a range of values that act as good estimates of the unknown population parameter. However, it is not unusual that none of these values covers the value of the concentration that must be quantified. A level of confidence of the confidence interval is chosen using chemical knowledge and know-how which are already at the disposal of chemists. This level of confidence indicates the probability with which the confidence range captures the "true" value of the quantity under consideration. This interval is calculated from the standard deviation characterizing the dispersion of the operational process. The statistical modeling of sets of data becomes of crucial importance for chemical inferences and should not be left aside in a philosophical study concerned with the *ceteris paribus* clause in chemistry.

[3] The ISO 5725 provides a procedure for obtaining intermediate measures of precision, basic methods for the determination of the trueness of a measurement method, the determination of repeatability and reproducibility of a standard measurement method.

Despite the fact that many factors do not cease to change, the mixture of bodies is gradually separated, the polarity of solvents is modulated, the flow rate can evolve as well as the temperature, and so on, but one thing must remain inside strict boundaries: The concentration of the bodies under study. *The ceteris paribus clause is about the possibility for a particular determination of a quantity to belong to a very short confidence interval, notwithstanding all the fluctuations which continue to occur*. This result is relative to the complex {apparatus-methods-bodies-associated milieu-devices} at stake. The same apparatus is not prepared in the same way according to the nature and the quantity of the body under investigation. The method of analysis is not used in the same way if the triad composed by the apparatus, the bodies, and the associated milieu has changed. In this context of activity, methods can never be blandly detached from the content it yields. The association between the apparatus and the method depends on the associated milieu, the device, and the bodies under study. The five elements of the complex are co-adapted to one another. If chemists change a factor, for example a type of column, the mode of injection of the solvents, the quantity of product, the matrix from which it is originated, the preparation of the sample, the detector, among other possibilities, they will have to resume the process of co-adaptation from the very beginning because the complex does not work anymore. For example, they know that a method validated for titrating pesticides in a certain type of lettuce cannot be used for quantifying the same pesticides in other varieties such as Batavia or escarole originated from the same agricultural site. In this case, the difficulty will be to choose a standard, namely a blank matrix, with *enough* representativeness in order to encompass the different empirical determinations available.

In short, chemists must stabilize *a specific domain of application* of the whole complex in order to determine a quantity of a particular type of body within certain limits imposed by standards of normalization and laws. The sentence "all things being equal" encompasses the co-adaptation and the channeling of multifarious fluctuations which, in turn, leads to the very possibility of making holistic inferences as regards the performance of the whole complex within the normative framework of a quality control process. The *ceteris paribus* clause is not illusory in the domain of chemistry but refers to a new type of "nomological machine," to use Nancy Cartwright's turn of phrase, that is

> a fixed (enough) arrangement of components, or factors, with stable (enough) capacities that in the right sort of stable (enough) environment will, with repeated operation, give rise to the kind of regular behavior that we represent in our scientific laws. (Cartwright 1999, p. 50)

The idea of nomological machine is interesting for our purpose insofar as it revolves around the key notion of co-stabilization. We nevertheless prefer to use the word preparation instead of that of arrangement. We also prefer to focus our work on the notion of a complex which displays certain type of *affordances* in the context of chemistry because the mode of access often takes part in the constitution of what chemists are studying and talking about. Following Bachelard's notion of 'phenomenotechnique' (1934), we assert that the question is not one of reality and

its knowledge – *that which is* – but rather one of 'realisation,' that is, *what can be*. Objectivity is not given from the beginning, but rather produced in a 'process of objectification,' the provisional result of which is a 'double instruction' of the world and human intelligence. With Bachelard again, we consider that the sciences themselves must be assessed as particular and concrete forms of life with different 'microrationalities' addressing quite different sets of problems and surrounding conditions, and which have their own awkwardness: 'Each interesting problem, each experiment, or even each equation requires a philosophical reflection of its own' (Bachelard 1940, p. 14). This is the reason why it is of paramount importance for us to investigate chemical practices in order to study the *local* meaning, if any, of the *ceteris paribus* clause in the 'canton' of chemistry. Without the multiplication of perspectives, there is no objectivity.

Because precision is sensitive to the way it is determined some specific types of precision should be distinguished. *Reproducibility* is the measure of agreement between results obtained with the same method on identical test or reference material under different conditions, executions by different persons, in different laboratories, with different equipment and at different times. The measure of reproducibility is the standard deviation of these results. *Repeatability* is the measure of agreement between results obtained with the same method on identical test or reference material under the same conditions, the job done by one person, in the same laboratory, with the same equipment, at the same time or with only a short time interval. Repeatability corresponds to the *ceteris paribus* clause as it is usually defined by logicians in domains different from chemistry. At this point of our enquiry, we understand that what is considered to be the meaning of the *ceteris paribus* clause in many contexts only corresponds to a single step among many others belonging to a long chain of procedures carried out for stabilizing what we call the complex {apparatus-methods-bodies-associated milieu-devices} in the framework of chemistry.

Chemists then resort to the study of the *within-laboratory reproducibility* which is the agreement between results obtained with the same method on identical test material under different conditions, execution by different persons, with the same or different equipment, in the same laboratory, at different times. This is a more realistic type of precision for a method over a longer span of time when conditions are more variable than defined for repeatability. Last but not the least along our non-exhaustive list, they have to ensure the *robustness/ruggedness* of an analytical procedure which is defined as a measure of its capacity to remain unaffected by small, but deliberate variations in method parameters and provides an indication of its reliability during normal usage. Such conditions can be temperature, extraction or shaking time, shaking technique, pH, purity of reagents, and sample size, among many factors. The ruggedness test is conveniently done with the so-called "Youden and Steiner partial factorial design" thanks to which analyses seven factors can be varied and analyzed in only eight replications. This test corresponds to another practice of modeling which holds probability, metrology, and chemistry together.

Each step of the co-stabilization of the whole complex reveals a certain amount of repetitions and holds a wide range of multifarious tools together. Concomitant

changes of factors, the use of many statistical tools and tests, the continuous modeling of results, and the use of normalization standards, do not cease to be at the forefront of this workaday practice. We shall not enter into more details and a lot of work remains to be done in the domain of the epistemology of chemical metrology, in particular as regards the way statistical methods are intertwined with chemical purposes for stabilizing domains of results which enable chemists' inferences. We cannot but be impressed by the hard and intensive work of co-stabilization of the different elements of the whole complex achieved by chemists. In the *Encyclopédie méthodique*, the chemist Louis Bernard Guyton de Morveau insisted on the 'composure' and the 'circumspection' that chemists must demonstrate in order to develop their protocols of synthesis and to validate their methods of analysis (Guyton de Morveau 1805, p. 575). Current quality control activities strengthen his statement.

14.4 Philosophical Conclusions

The situation we have previously described is somewhat different from the case of an apparatus, for example a voltmeter, which only needs to be connected to any electrical circuit provided, of course, that the voltage is measurable by the voltmeter at hand. The stabilization of the complex, the reliability of this stabilization, and the determination of the unknown quantity are at stake within the ongoing process, they are precisely that which chemists must reach: They are not "given." The *ceteris paribus* clause gets a *pragmatic meaning* related to the result of an analysis stemming from a prepared complex.

The clause ceases to be a premise or a metaprinciple which would be available independently of the situation. Rather, it acquires the epistemological status of a result of a long series of articulations and stabilizations; a result which, once obtained, makes it possible for chemists to validate or not to validate the quantification whenever all but the quantity of the body under investigation is channeled by co-stabilization. The *ceteris paribus* clause thus gets a meaning in chemical metrology, but this meaning is different from that used in logic or within the framework of the deductive and nomological reasoning proposed by Hempel (1966). It has been *transformed* and not simply *transposed* from a particular sphere of scientific activity or human inference to another. The clause becomes a heuristic tool for innovation and action that can be connected to ethical purposes in order, for instance, to control and replace bad consequences of uses of chemicals by sustainable ones.

The meaning of a clause or a premise can indeed be transformed depending on the scientific 'canton' involved insofar as many principles, assumptions, theoretical tools, complexes in the sense that we previously defined, and the axioms that it encompasses, are themselves transformed, and take another semantic, operative, and technological meaning. We should take the couple {scientific and technological preparation-ontological assumptions associated to them} into account in order to

investigate human inferences and not exclusively scientific languages or apparatus. A 'phenomenotechnique' is always related to ontological assumptions within the context of a background culture. Putnam has shown that neither concepts nor the most basic categories are unique, unavoidable or absolute: 'The logical primitives themselves, and in particular the notions of object and existence, have a multitude of different uses rather than one absolute "meaning".' (Putnam 1987, p. 19) We claim that it is the same situation for allegedly cross-context premises, postulates, and clauses. With Meyerson (1921), we point out the role of ontology in scientific reasoning; knowing that this ontology depends on a background language. Following Quine (1981) and the later Wittgenstein, we aim to anthropologize logical and nomological spheres, but with the specific approach that consists in developing a distributed epistemology focused on instrumentation and materials.

The "object" targeted by the clause is not a pre-constituted particular with intrinsic properties, but rather an affordance, in Harré's sense (1986), the constitution of which depends both on the mode of access and the world. The fact that affordances can be reified or considered to be a useful and heuristic concept for studying sciences does not change this conclusion. The object, the meaning, and the status of the *ceteris paribus* clause are partly dependent on the representation we share about sciences, language, apparatus, and the world. They also depend on mereological strategies. To dissociate the complex, the measurement, the body, the methods, the associated milieu, and the devices, as if their role were understandable in isolation, is a fragmentation that echoes the mereological assumption that the information related to a whole is not lost when the whole is segmented into parts. If, by contrast, we study all those elements from a holistic standpoint, we develop a synthetic reasoning which consists in following another mereological slope. Both approaches are useful and neither is sufficient. It is the articulation between the two that is required in order to reflect upon the condition of inferences from comparison. This is the reason why a distributed epistemology focused on scientific methodology, apparatus, and materials is of importance and remains complementary to analytical studies of reasoning and languages. Relativism can be avoided by a 'distributed' epistemology of chemical 'cantons.' Deleuze once asserted: 'It is not the variation of truth with the subject, but the condition under which appears to the subject the truth of a variation' (Deleuze 1988, p. 27).

Both the complex {apparatus-methods-bodies-associated milieu-devices} and the group of chemists charged with the validation of the result of the sample analysis co-emerge from the stabilization procedure. The final complex, the quantification itself, the group of chemists guided by these standards, chemical knowledge and know-how can only be defined and described *together*, despite the presence of standards and formal rules which guide the action rather rigidly from the outset. It is the whole complex and its associated group of chemists that change and become a condition of possibility of the study of future variations. Once the co-stabilization is reached, the truth of the studied variation is validated with a certain degree of confidence. This story is not about the "dissolution" of the truth but, by contrast, deals with the "co-constitution" of the subject-object polarity.

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